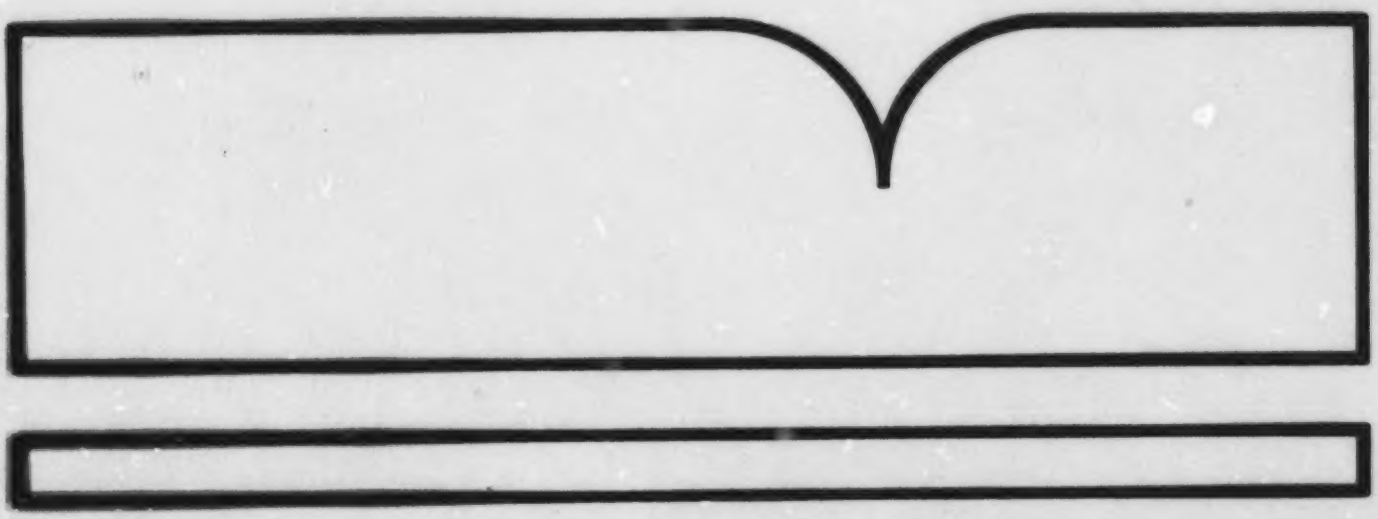
PB86-233186

Development of Land Disposal Decisions for Metals Using Minteq Sensitivity Analyses

(U.S.) Environmental Research Lab., Athens, GA

Aug 86



U.S. Department of Commerce
National Technical Information Service

PB86-233186

EPA/600/3-86/030
August 1986

DEVELOPMENT OF LAND DISPOSAL DECISIONS FOR METALS USING MINTEQ SENSITIVITY ANALYSES

by

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ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
ATHENS, GA 30613

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA/600/3-86/030		PB86-233186/AS

4. TITLE AND SUBTITLE	5. REPORT DATE
DEVELOPMENT OF LAND DISPOSAL DECISIONS FOR METALS USING MINTEQ SENSITIVITY ANALYSES	August 1986
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
David S. Brown, Roger E. Carlton, and Lee A. Mulkey	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Environmental Research Laboratory U.S. Environmental Protection Agency Athens, GA 30613	ABWD1A
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Research Laboratory - Athens, GA Office of Research and Development U.S. Environmental Protection Agency Athens, GA 30613	14. SPONSORING AGENCY CODE EPA/600/01

15. SUPPLEMENTARY NOTES

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	72
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	$ 11.95

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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FOREWORD

As environmental controls become more costly to implement and the penalties of judgment errors become more severe, environmental quality management requires more efficient management tools based on greater knowledge of the environmental phenomena to be managed. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Assessment Branch develops simulation techniques for predicting pollutant behavior.

In contrast to many organic pollutants, metals undergo a variety of complex speciation reactions in the environment. Many metals can exist in several oxidation states simultaneously and form a number of individual species of widely differing chemical characteristics. In this report, a screening procedure is described for predicting the transport potential of metals in the dissolved phase in groundwater.

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ABSTRACT

Procedures were developed for estimating the impacts of metal speciation reactions on the potential transport of metals through groundwater to a measurement point directly down gradient from a land disposal unit that has failed. The primary emphasis was on simultaneous solution of metal speciation reactions that determine the dissolved phase. The metals considered were arsenic, barium, cadmium, lead, nickel, thallium, chromium, mercury, selenium, and silver.

This report covers a period from june 1, 1985, to April 30, 1986, and work was completed as of April 30, 1986.

CONTENTS

1. Introduction. 1
   1.1 Background 1
   1.2 Relationship to Organic Wastes-Back Calculation 2
   1.3 Basic Assumptions 7
   1.4 Rationale for Speciation Model 8

2. Metal Speciation Model (MINTEQ) 9
   2.1 Origin and Documentation of MINTEQ 9
   2.2 Data Base Supplements 10
   2.3 MINTEQ Component Expansion 10
   2.4 Numeric Underflows 11

3. Treatment of Variability 11
   3.1 Generic Background Chemical Specifications and Uncertainty Window 11
   3.2 Added Metal Mixing Scenario 17

4. Other MINTEQ Procedures 19
   4.1 Solids Selection 19
   4.2 Treatment of Metal/Organic Interactions 21
   4.3 Criteria for Omitting Treatment of Metal Sorption 25

5. Cautions and Problem Areas 25
   5.1 Specific Nature of Speciation Processes 25
   5.2 Kinetic Limitations 26
   5.3 Imperfections in the Data Base 27

6. Results 27
   6.1 Reporting Format 27
   6.2 Interpretations/Recommendations for the Mobile Metals Group 31

7. References 44

Appendix. Worst Case Concentrations for Ten Metals . . . 46

1. INTRODUCTION

1.1 Background

The U.S. Environmental Protection Agency often has the responsibility for dealing with pollutants in situations where the specific environment available for interaction with the pollutant at each individual site is unknown. In these cases the decision process must necessarily involve a generic component. Typical examples are the Office of Toxic Substances' efforts in evaluating Premanufacturing Notices for new chemicals and development of regulations governing underground storage tanks. This report outlines a generic approach for evaluating the speciation and transport of metals in groundwater environments that may be relevant to these problems. The primary emphasis was on the simultaneous solution of metal speciation reactions that determine dissolved phase metals concentrations.

Ten metals including arsenic, barium, cadmium, chromium, lead, mercury, nickel, selenium, silver, and thallium are considered. Speciation and transport of these metals in groundwaters are considered in an example setting designed to mimic the behavior of the leachate from a failed land disposal site. The procedures used are designed to be fully compatible with the recently proposed methods for treatment of organic leachates (1). The advective dispersion model is used directly except that the degradation parameters are set to zero for metals. Also, because the metal speciation model is computationally intensive, a full monte carlo analysis was not feasible. Real variations in site-specific chemical backgrounds relative to the presumed generic groundwater chemical environment were accommodated using an uncertainty window approach. The uncertainty window was developed from statistical data on pH and redox conditions (E_h) reported for existing wells around the country. Because

the E_h conditions were not well known, supplemental speciation model sensitivity tests for redox conditions outside the original uncertainty window were also performed. These were necessary to better define the transition between solid and dissolved phases for selected metals.

1.2 Relationship to Organic Wastes--Back Calculation Procedure

It is instructive to consider the overall back-calculation procedures proposed for screening organic chemicals in groundwaters. These methods also are used for metals, but with the addition of a metal speciation model component. Figure 1 schematically illustrates a presumed failed land disposal unit, the underlying aquifer, the waste leachate plume and the down gradient well. Simply stated, the goal of the screening procedure is to establish health-based concentration thresholds applicable to extracts of the raw waste that are assured of being protective of human health and the environment at the down-gradient exposure point (drinking water source). Health-based concentration thresholds (C_{ADI}) applicable to the point of exposure serve as the starting point. These are determined (apportioned) such that exposure to other sources (surface water, air) are taken into account. Elaboration of the detailed conceptual approach used in establishing the C_{ADI}'s is available in the Code of Federal Regulations (1). For the purposes of this discussion, it is sufficient to view the C_{ADI} as the pollutant concentration corresponding to the maximum allowable daily intake of a person using the down gradient well as a drinking water source.

The basic problem of the screening procedure is to utilize the C_{ADI} to back calculate allowable raw leachate concentrations at the point of entry into the aquifer. Leachates are mimicked by the pollutant concentration observed in an extract of the raw waste material (1). A

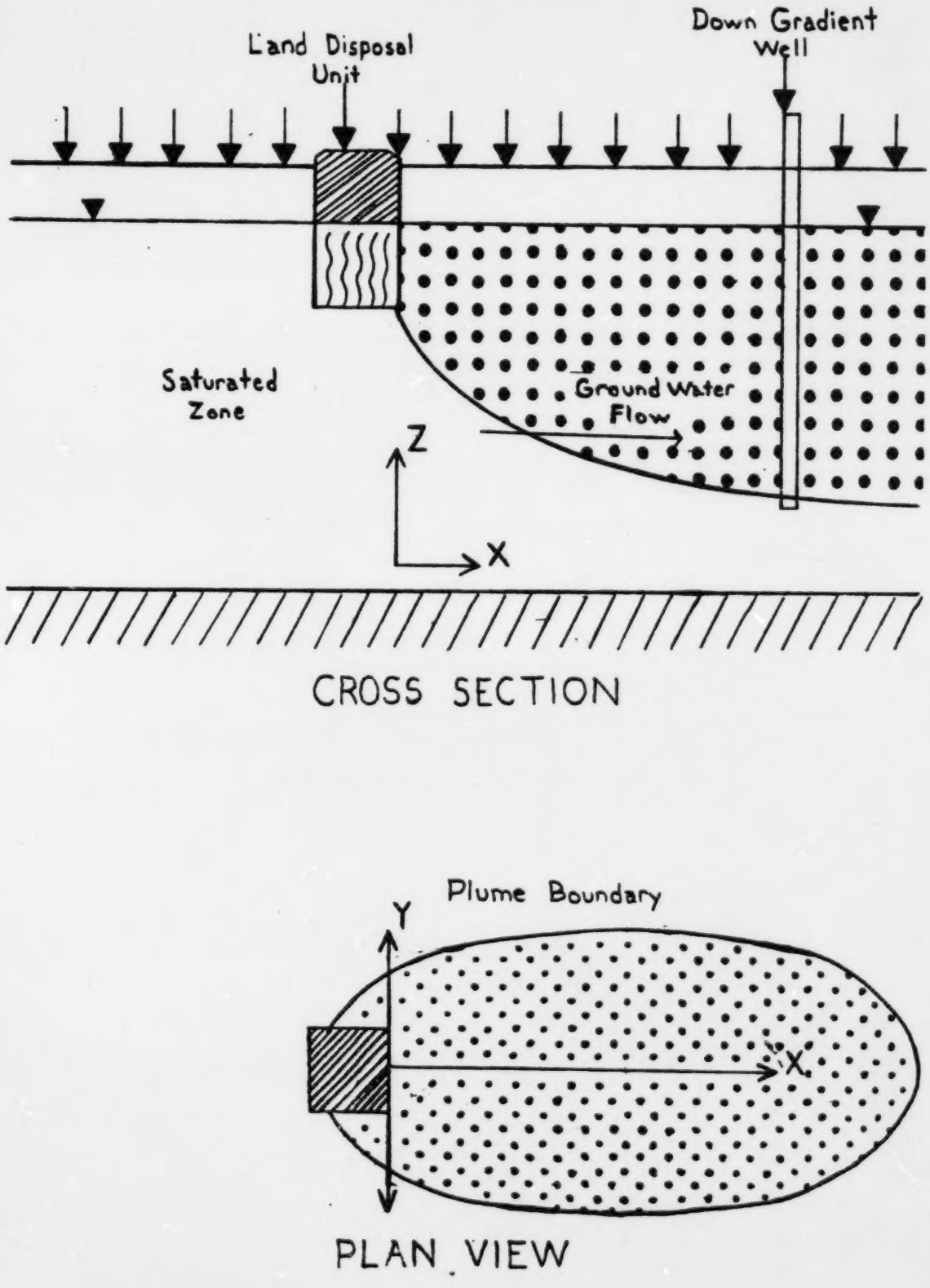


Figure 1. Schematic representation of plume from a failed waste disposal unit.

three-dimensional steady-state advective-dispersion model that has an analytical solution is used to calculate allowable concentrations in the extract using C_{ADI} at the receptor well as input. The dispersion model (Equation 1) utilizes a Gaussian boundary condition and accounts for chemical specific decay and velocity consistent with a number of assumptions.

$$D_{xx}\frac{\partial^2 c}{\partial x^2} + D_{yy}\frac{\partial^2 c}{\partial y^2} + D_{zz}\frac{\partial^2 c}{\partial z^2} - \frac{V}{R_f}\frac{\partial c}{\partial x} = \frac{\partial c}{\partial t} + \lambda c + Ic \qquad (1)$$

where:

x,y,z = spatial coordinates in the longitudinal, lateral, and vertical directions, respectively (m)

c = dissolved concentratin of chemical (mg/l)

D_{xx}, D_{yy}, D_{zz} = retarded dispersion coefficients in the x, y and z direction, respectively (m^2/yr)

V = groundwater seepage velocity assumed to be in the x direction (m/yr)

R_f = retardation factor (dimensionless)

t = elapsed time (yr)

λ = effective first order decay constant (yr^{-1})

θ = volumetric water content of the porous medium (cm^3/cm^3)

I = dilution rate due to net recharge (yr^{-1})

The retardation factor, R_f, and the effective decay constant, λ, are defined as follows.

$$R_f = 1 + \frac{\rho_b K_d}{\theta} \qquad (2)$$

and,

$$\lambda = \frac{\lambda_1\theta + \lambda_2 \rho_b K_d}{\theta + \rho_b K_d}$$

where:

P_b = bulk density of the porous medium (g/cm^3)

K_d = distribution coefficient (cm^3/g)

θ = volumetric water content (cm^3/cm^3)

λ_1 = decay constant for dissolved phase (yr^{-1})

λ_2 = decay constant for sorbed phase (yr^{-1})

Several assumptions regarding the medium and the chemical behavior of the wastes are incorporated into the dispersion model (3). These include:

(1) Saturated soil conditions (no attenuation of chemicals in the unsaturated zone).

(2) Flow regions of infinite extent in the longitudinal direction, semi-infinite extent in the lateral direction, and finite in the vertical direction.

(3) All aquifer properties are homogeneous and isotropic and of constant thickness.

(4) Groundwater flow is uniform and continuous in direction and velocity.

(5) Degradation is limited to hydrolysis and byproducts of hydrolysis are assumed to be nonhazardous.

(6) Sorption behaves linearly.

(7) Infinite source--supplies a constant mass flux rate.

(8) Precipitation recharge supplies water to the aquifer.

(9) The groundwater is initially free of contamination.

(10) The receptor well is directly in line with the source and the groundwater flow.

(11) The receptor well is located 500 feet from the unit.

Because the behaviors of individual waste constituents are highly dependent on the chemical properties of the compounds as well as on the input variables relating to the transport environment, selection of "reasonable worst case" values would involve considerable uncertainty. To avoid this ambiguity, a Fortran computer code, EPASMOD-P, was developed for the dispersion model that allowed monte carlo simulation of the input parameter distributions. Back-calculated concentration values were determined for a large number of combinations of the input variables (typically 5000) randomly selected from the independent and dependent distributions. Known or expected dependencies among the input variables were accommodated in the process of developing input distributions. Results were expressed as a distribution of back calculated allowable leachate concentrations keyed to relative probabilities of occurrence. Final selection of the regulatory concentration would involve a policy decision regarding relative risk. The resulting concentration is the level that must not be exceeded in the extract of the raw waste. Where treatment is possible the treated waste product would be subject to the same test.

The transport model is also used for metals. There are, however, some important additions and exceptions:

1) Metals are assumed to be conservative entities and degradation due to hydrolysis is not allowed, i.e., $\lambda = 0$. (This does not preclude treatment of metal hydrolysis reactions in the speciation model.)

2) The MINTEQ (2,3) metal speciation model is employed to account for reductions in dissolved metals concentrations resulting from speciation reactions that result in precipitation of solids from the waste leachates entering the groundwater.

3) The selection of sorption parameter (K_d) values for conservative entities (metals) influences only the retardation times and not the concentrations of pollutants predicted to arrive at the down gradient well. This follows from the infinite source, steady state character of the dispersion model. No attempt was made to account for sorption of metals in the groundwater matrix.

4) The metal speciation model code involves the Newton-Raphson numeric solution technique and is not amenable to closed-form analytical solution. For this reason it was not directly coupled to the dispersion model. Total dissolved metals concentrations determined from the MINTEQ outputs could be plotted as a function of input metal concentrations to provide overall attenuation factors necessary to carry out the back-calculation required in the screening plrocedure.

1.3 Basic Assumptions

Several assumptions guided the development of the proposed screening approach for metals:

1. Metals exist in groundwater environments as distributions of multiple, dissolved-phase species and precipitated solids.
2. All dissolved species are freely mobile and available for transport as implemented by the dispersion model.
3. All precipitated metal species are immobile.
4. Metals (excluding radionuclides) are conservative (non-degrading) entities.
5. Overall metal speciation distributions are sensitive to properties of the subsurface environment, including pH, redox status and

dissolved solutes.

6. pH and E_h of the receiving groundwaters are effectively buffered against changes caused by introduction of the leachate.

7. Transport of individual metal species is governed by the specific properties of that species (mobile versus immobile); however, individual species are related to each other through the equilibrium constants controlling speciation reactions.

The main thrust was to develop a generic screening procedure for metals that was compatible with the treatment of organics and consistent with these assumptions. The primary emphasis was on estimating the reduction in dissolved metal concentrations in the leachate plume due to precipitation of solids in the groundwater.

1.4 Rationale for the Speciation Model

In contrast to many organic pollutants, metals undergo a variety of complex speciation reactions. The result is that each metal will exist in the subsurface environment as a relatively complex distribution of different species, each having a specific set of properties. Relative concentrations of individual species within the distribution are controlled by equilibrium constants governing the speciation reactions and by the chemical environment in which the speciation process occurs. Many metals can exist in several oxidation states simultaneously and form a number of individual species of widely differing chemical characteristics.

These chemical and physical characteristics were considered paramount in determining the potential for transport. An attempt was therefore made to quantitatively model the geochemical behavior of metals in spite of the recognized uncertainties inherent in doing so. An organized analysis using

current speciation modeling techniques was judged preferable to making an oversimplified guess or simply failing to address the problem. Speciation reactions that reduce solution phase metals concentrations most directly influence the potential for transport in groundwater. The basic premise of the proposed screening procedure (and hence the choice of the speciation approach) is that significant metals transport occurs only in the dissolved phase.

2. METAL SPECIATION MODEL (MINTEQ)

2.1 Origin and Documentation of MINTEQ

Estimates of metals species distributions are determined using the geochemical model MINTEQ (2,3). MINTEQ uses the equilibrium constant approach to solving the chemical equilibrium problem. The mathematical structure is from MINEQL (4) and the original thermodynamic data base was from WATEQ3 (5). Several additions to the data base were required for work on the proposed screening procedure. These are discussed later. MINTEQ also has been coupled to the aquatic exposure assessment model EXAMS (6) to form the Metals Explosure Analysis Modeling System (MEXAMS). Only the MINTEQ part of the MEXAMS program is used in the present analysis, but the MEXAMS users manual (3) is a useful reference for MINTEQ users.

Earlier versions of MINTEQ were enhanced by the interactive preprocessor routine MISP, which assist in developing complex input data sets. Current versions of MINTEQ incorporate the improved preprocessor code PRODEF (7), which permits interactive error recovery and assists in avoiding common errors such as loading input sets which would result in phase rule violations. It should be noted that the preprocessor codes are not an integral part of the MINTEQ code. Experienced users will likely find

assembling their own input data sets for direct use by the main program more efficient. Frequently, the assemblage of a new input data set can be accomplished by editing a few lines from some previous input set.

Because the previously existing MINTEQ code would not accommodate more than 20 input components, dimensional expansions of the code were necessary to facilitate the present effort. Since the original data base did not cover reactions for mercury, chromium, selenium and thallium, supplemental data for these metals had to be added. These and other modifications are described in the following sections.

2.2 Data Base Supplements

Supplemental thermodynamic data for mercury, chromium, thallium and selenium were provided through Work Assignment No. 29, EPA Contract No. 68-01-6986 with Battelle, Pacific Northwest Laboratories, Richland, Washington. Results are reported in "MINTEQ Geochemical Code: Compilation of Thermodynamic Database for the Aqueous Species, Gases and Solids Containing Chromium, Mercury, Selenium, and Thallium" by W. J. Deutsch and K. M. Krupka (8). Because of time constraints, complete critical reviews of the supplemental data were not possible. For this reason the new data should be regarded as preliminary even though every effort was made to select from the best available sources.

2.3 MINTEQ Component Expansion

The original MINTEQ code was dimensioned to handle 20 components. This proved inadequate for the screening procedure and dimensional expansions were put in place to facilitate investigating more complicated systems. The modified code will now accommodate 50 components. Because the original code was not written with general parameter statements, it had to be rewritten

in that form to facilitate the component expansion. Matrix alignment difficulties would have otherwise resulted.

2.4 Numeric Underflows

Depending on the specific hardware used, early versions of MINTEQ frequently produced numeric underflows that caused the program to abort when individual component concentrations became very low (10^{-30} mol/ℓ). To eliminate this problem, checks were put in place to detect the occurrence of very low component concentrations during calculations. When they did occur, the component concentration was set equal to a limit of 10^{-30} and the execution allowed to continue. This change is easily noticed in MINTEQ outputs. The percentage distribution of components listing will show equal percentages for several species listed under a given component if the component was subject to the low concentration limit correction. Users should interpret these listings accordingly.

The present source code distributed by the EPA Center for Water Quality Modeling reflects all the additions and modifications outlined here and in Sections 2.2 and 2.3.

3. TREATMENT OF VARIABILITY

3.1 Generic Background Chemical Specifications and Uncertainty Window

Operating under the constraint that a site specific modeling approach to the groundwater screening protocol was not tenable from the regulation standpoint, generic groundwater chemical specifications were developed. The goal was to assemble a set of chemical specifications that reflected a national median groundwater chemical environment. This was accomplished by extracting large volumes of data tabulated for well waters in the EPA STORET (9) data retrieval system. Background analytical concentrations of

the ten waste metals were considered along with concentrations of several key anions, organic carbon contents, E_h, and pH. Maxima, minima, medians, means, standard deviations and several representations of the frequency distributions were recorded for each variable listed in Table 1. The wide variations in observed groundwater chemical specifications are reflected in the tabulation in Table 1. Mean values were strongly influenced by a few extreme values. For this reason, median values were used in establishing generic groundwater specifications. The final specifications consisted of the median values for all variables except E_h and pH which were varied systematically to establish an "uncertainty window."

Obviously, a single set of generic specifications could not be selected that would accurately reflect conditions existing at all waste sites. Indeed, a single set of specifications would probably not be adequate for a given waste site over a period of time. For this reason, an uncertainty window encompassing a range of E_h and pH values was defined. Speciation equilibria calculations were performed repeatedly using several E_h and pH combinations in conjunction with the median values of other variables tabulated in Table 1. Total dissolved metal concentrations were calculated for each combination. The universal influence of E_h and pH on the overall speciation equilibria was reflected in the matrix of values obtained.

This approach to the uncertainty problem generated by using generically derived input sets differs from the monte carlo sensitivity analysis used in other parts of the screening procedure in that pH and E_h were the only variables tested. Given the computationally intensive nature of MINTEQ and the infinite set of possible background chemistries, a full monte carlo analysis was not possible.

Table 1. Median Groundwater Chemical Specifications

Component	Analytical Concentrations (mg/l) Mean	Stand. Dev.	Median
Arsenic	.021	.174	.010
Barium	.235	.251	.200
Cadmium	.030	.207	.005
Chromium	.044	.121	.200
Lead	.035	.078	.010
Mercury	.0006	.0008	.0005
Selenium	.007	.008	.005
Silver	.019	.030	.010
Thallium	.068	.037	.010
Aluminum	1.134	2.620	.200
Calcium	79.000	118.478	48.000
Iron	2.780	7.365	.200
Magnesium	51.240	134.840	14.000
Manganese	.242	.615	.040
Potassium	5.670	11.390	2.900
Sodium	182.610	642.780	22.000
Bicarbonate	189.730	111.000	190.000
Bromide	3.400	12.800	.300
Carbonate	22.300	30.037	0
Chloride	161.470	778.530	15.000
Nitrate	2.660	5.100	1.000
Phosphate	1.450	5.210	.090
Sulfate	153.810	347.350	25.000
Sulfide	.471	1.334	.200
Organic carbon	12.762	15.603	7.2
Temperature (°C)	14.403	5.287	14
pH	6.621	1.285	6.8
E_h (mv)	-10.535	155.786	-50

The dimensions of the uncertainty window (Figure 2) were fixed at one standard deviation (from the mean) either side of the median E_h and pH values. Thus, the window dimensions were $pH_m - \sigma_p \leq pH \leq pH_m + \sigma_p$ versus $E_h^m - \sigma_E \leq E_h \leq E_h^m + \sigma_E$.

where: E_h^m = median E_h = -50 mv

pH_m = median pH = 6.8

σ_E = standard deviation of E_h = 156 mv

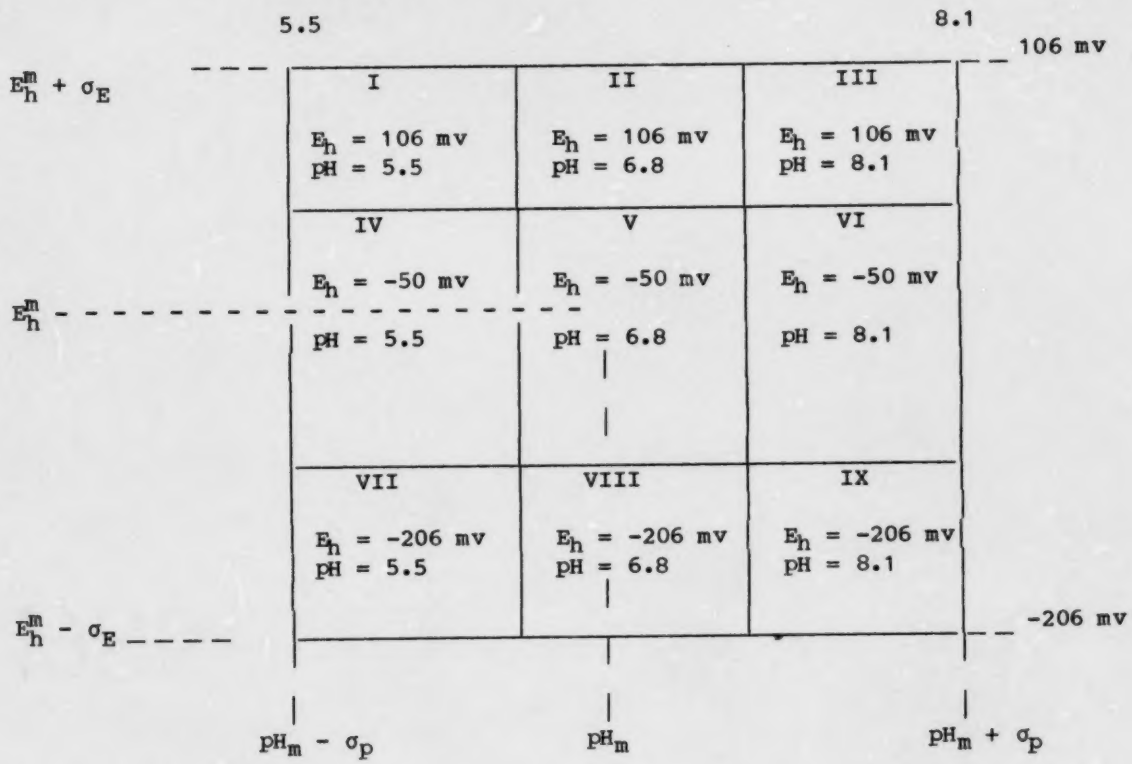
σ_p = standard deviation of pH = 1.3

Shifts in metal speciation equilibria possible within the window were mapped by initiating MINTEQ model calculations using the nine different E_h and pH combinations illustrated schematically in Figure 2. These nine E_h, pH pairs were formed by pairing three values each of E_h and pH in all possible ways. The E_h and pH values used in the combinations were:

E_h	pH
E_h^m = -50 mv	pH_m = 6.8
$E_h^m + \sigma_E$ = 106 mv	$pH_m + \sigma_p$ = 8.1
$E_h^m - \sigma_E$ = -206 mv	$pH_m - \sigma_p$ = 5.5

Figure 3 illustrates how the uncertainty window relates to the environmental pH range of 4 to 9 and the stability of water as defined by the lines where it is either oxidized to O_2 or reduced to H_2 according to equations 3 and 4 (10).

Figure 2. E_h, pH Uncertainty Window



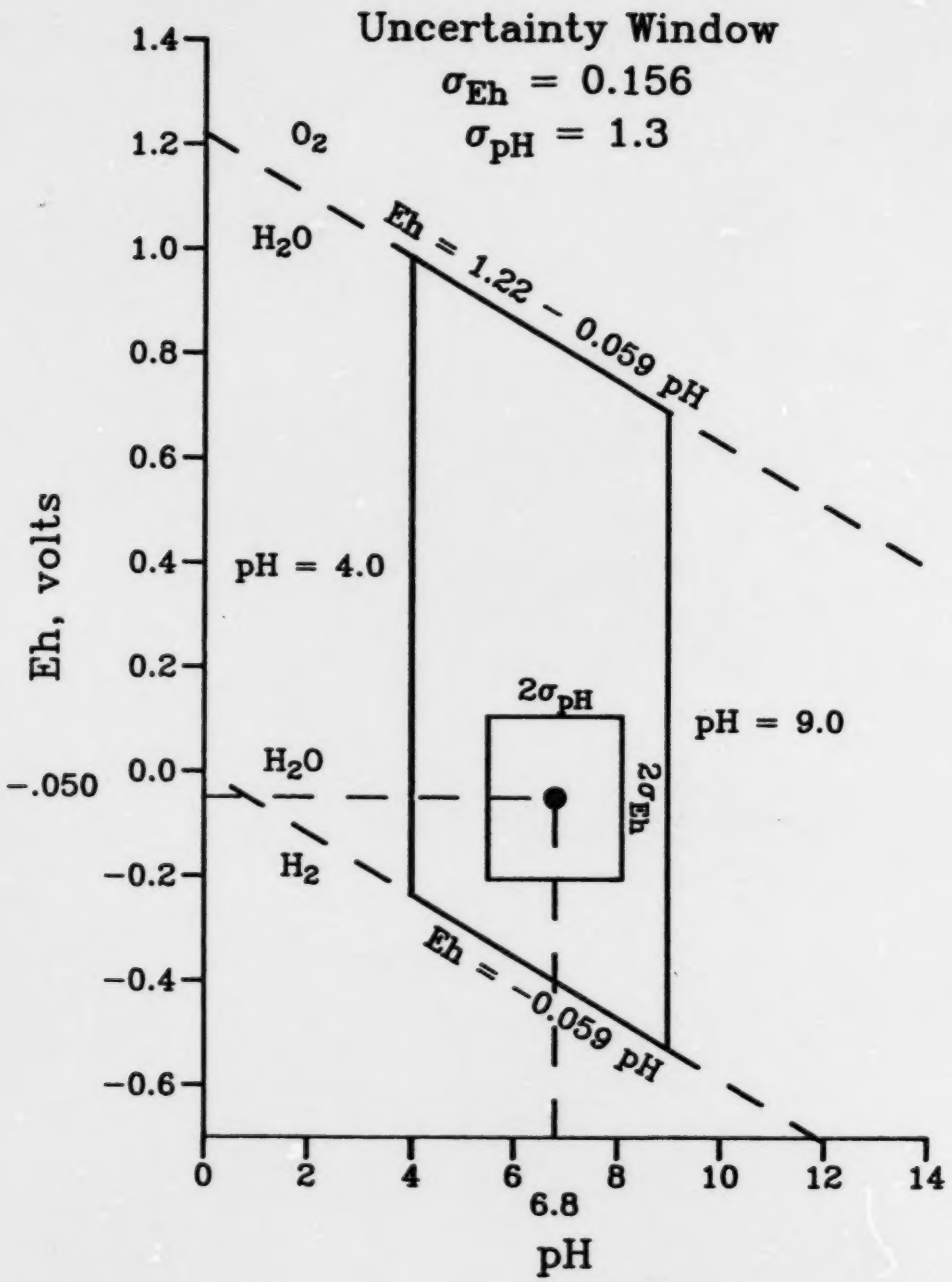


Figure 3. Uncertainty window relative to possible environmental conditions.

$$H_2O \rightleftharpoons 1/2\ O_2 + 2H^+ + 2e^- \qquad E^\circ = +1.23v$$

$$E = 1.23 + \frac{0.059}{2} \log [O_2]^{1/2} [H^+]^2$$

for $P_{O_2} = 0.2$ (3)

$$E_h = 1.23 + 0.030 \log (0.2)^{1/2} + 0.059 \log [H^+]$$

$$= 1.22 - 0.059\ pH$$

$$H_2 \rightleftharpoons 2H^+ + 2e^- \qquad E^\circ = 0.00v$$

$$E = \frac{0.059}{2} \log [H^+]^2 - \frac{0.059}{2} \log [H_2]$$

$$= -0.059\ pH - \frac{.059}{2} [H_2]$$

for $P_{H_2O} = $ max. of 1 atm (4)

$$E_h = 0.059\ pH - \frac{0.059}{2} \log (1)$$

$$= -\ 0.059\ pH$$

3.2 Added Metal Mixing Scenario

The uncertainty window does not address variations in the mixing ratios of individual metal input components. A full monte carlo analysis of all the variables was not feasible due to the computationally intensive nature of the speciation model. Since some of the metals investigated were capable of forming precipitates with each other, the probability of solid formation was considered maximized when all ten metals were added simultaneously. Alternatively, the maximum dissolved phase metal concentrations

would be expected if each metal was added individually to the background generic matrix. Since this latter alternative represented the environmentally conservative assumption, each of the ten metals was added individually, in the following sequence of concentrations:

a) DWS + median background metal concentration

b) 25 times DWS

c) 50 times DWS

d) 100 times DWS

e) 10,000 times DWS

where DWS = current drinking water standard concentrations listed in Table 2.

Table 2. Current EPA Drinking Water Standards

Metal	Concentration (mg/l)
Arsenic	0.050
Barium	1.500
Cadmium	0.005
Chromium	0.120
Lead	0.020
Mercury	0.003
Nickel	0.150
Selenium	0.045
Silver	0.090
Thallium	0.019

Median background concentrations of the other nine test metals were also present in each system modeled. All nine E_h/pH combinations defined by the uncertainty window were investigated for each metal. The worst case (defined by highest total dissolved concentration for each metal in the MINTEQ output) was selected from the collection of data from all model runs. This defined a worst case E_h/pH combination.

4. OTHER MINTEQ PROCEDURES

4.1 Solids Selection

Because of the complex nature of the speciation mixtures investigated, formation of a large number of solids was possible. To avoid complicating the speciation calculations past the point of manageability, only those solids that were known to supersaturate (under at least some of the E_h/pH combinations) and that contained one of the ten test metals or a key anion known to interact strongly in terms of potential solid formation were considered. To arrive at the final solids list, a series of "solution chemistry only" model runs was performed with no solids selected.

In these systems, all ten metals were added (maximum possibility for solid formation) to the generic background at concentrations of 100 times DWS. Model runs were repeated at each of the nine E_h/pH combinations defined by the uncertainty window. The log saturation index listings in the MINTEQ outputs were consulted for the list of potentially supersaturated solids. These were distinguished by log saturation indices greater than zero.

The resulting cumulative list is shown in Table 3. The master list in Table 3 was then screened for solids that contained one or more of the ten test metals or key anions. Solids that did not meet these

Table 3. Solids Selection Chart
Condition: 10 Metals (100 X DWS) plus matrix
Log Saturation Indices

pH / E_h (mv)	Mineral name and I.D. No.	6.8, -50	6.8, -206	6.8, 106	5.5, -50	5.5, -206	5.5, 106	8.1, -50	8.1, -206	8.1, 106
6003001	$Al(OH)_{10}SO_4$	3.111		3.110	3.118		3.120			
6010000	Barite	3.237		3.235	3.232		3.233	3.238	3.239	3.238
2003001	Boehmite	1.438	1.438	1.438	.792	.798	.792	1.257	1.257	1.257
2003002	Diasphore	3.242	3.242	3.241	2.595	2.602	2.596	3.060	3.060	3.060
4128100	$Fe(OH)_{2.7}Cl_{.3}$	.561		3.303				4.064	1.322	6.673
2003003	Gibbsite	1.388	1.389	1.388	.742	0.748	.742	1.207	1.207	1.207
3028100	Hematite	4.330		9.814			2.022	12.116	6.632	17.335
3028000	Magnetite	4.022		9.505				14.401	8.919	19.486
5016000	Otavite	1.732		1.731				2.753	2.753	2.753
7060001	Clypyromorph	13.655		13.653	10.242		10.241	12.053	12.053	12.054
7060002	Hyxpyromorph	2.221		2.220				1.920	1.920	1.921
7060003	Plumbgummite	7.209	1.225	7.208	6.440	1.938	6.440	3.439	3.439	3.438
7060007	$Pb_3[PO_4]_2$	1.608		1.607				.975	.975	.975
3028001	Hercynite	.245		.244				2.476	2.477	2.343
76000	Se, hex. blk.	7.972	2.487	8.405	6.665	1.180	12.151	9.271	3.786	1.108
76001	Se(A)	7.352	1.867	7.785	6.045	.560	11.531	8.651	3.166	.488
1228001	Ferroselite	15.4	9.267	10.779	12.790	7.307	18.275	17.992	12.508	
1260000	Clausthalite	17.879	11.894	12.826	17.324	12.804	17.324	17.875	17.876	4.226
1202000	Ag_2Se	7.022	7.022	7.022	7.022	7.022	7.022	7.022	7.022	7.022
1216000	CdSe	14.865	6.872	9.811	13.579	7.754	13.627	15.771	15.771	2.121
1228000	FeSe	3.479	2.831		2.175	2.177	2.174	4.771	4.773	
36000	Hg (l)	.793	0.600	.793	.793	.793	.793	.793	.793	.793
3021100	$FeCr_2O_4$	13.864	13.221	13.863	6.997	7.011	6.997	18.529	18.530	18.397
3021101	$Mg\ Cr_2\ O_4$	2.664	2.680	2.662				7.329	7.331	7.329
3021102	Cr_2O_3	8.726	8.732	8.726	4.456	4.469	4.456	10.798	10.798	10.798
2021102	$Cr(OH)_3$(A)	3.575	3.578	3.575	1.440	1.447	1.440	4.611	4.611	4.611
2021101	$Cr(OH)_3$(C)	.925	.928	.924				1.961	1.961	1.961
1028000	FeS PPT		.335							
1028001	Greigite		3.103							
1028002	Mackinawite		1.068							
1016000	Greenockite		5.427		5.357	5.208			6.097	
1060001	Galena		6.318		4.971	6.126			4.071	
1054000	Millerite		6.495		5.761	4.612				
1006000	Orpiment		22.212			22.790				
1006001	Realgar		2.345			3.838				
7210000	$Ba_3(AsO_4)_2$	15.184	4.222	22.029	2.194			25.050	17.168	25.075
1254000	NiSe	15.368	15.372	10.315	14.577	14.590		15.412	15.413	1.762
1036100	Cinnabar		6.518		4.112	4.303				1.572
1036101	Metacinnabarite		6.126	6.127	3.721	3.911				1.180
2028102	Geothite			2.426				3.577	.835	6.186
3028101	Maghemite			.286				2.588		7.807
5060000	Cerrusite	0.870		.869				.982	.982	.982
5060003	Hydcerrusite	0.205		.204				1.727	1.726	1.726
3028102	Lepidocrocite			1.961				3.112	.370	5.722
1028003	Pyrite		10.650		.618	6.478				
5015000	Aragonite							.214	.216	.214
5015001	Calcite							.392	.393	.392
5015002	Dolomite							.396	.398	.396
2028100	Ferrihydrite									2.194
2028101	$Fe_3(OH)_8$									4.388
5010000	Witherite							.541	.543	.541
2060004	$Pb(OH)_2$							.293	.292	.293
2054000	$Ni(OH)_2$							.691	.691	.691
7047001	$MnHPO_4$(C)							.250	.252	.251
3046001	Mag-Ferrite							3.122		8.340
1287000	Tl_2Se							.330	.332	
1087000	Tl_2S		0.226							
1002000	Acanthite		-0.150							

criteria were eliminated. Common examples of discarded solids were gibbsite, diaspore, boehmite, hematite, goethite, calcite, dolomite, aragonite, etc. The reasoning was that these should be at equilibrium with their respective groundwaters anyway and were the result of constructing generic groundwater specifications. Under the fixed E_h/pH combinations modeled they would not be expected to affect the results significantly.

Lists of solids relating to each metal are given in Table 4. It should be noted that these master lists include the possibilities represented by all nine E_h/pH combinations. Usually only one to three solids containing a given metal precipitated at any particular combination of E_h and pH. All solids shown in Table 4 were selected for possible precipitation in all the final MINTEQ model runs even though many of them were not expected to precipitate at a given E_h/pH combination.

4.2 Treatment of Metal/Organic Interactions

Little information is available on the kinds and amounts of organic materials present in typical waste site leachates. This information, along with appropriate thermodynamic data on the complexes with metals would be required to precisely estimate the impact of organics on overall metal speciation equilibria. Leachates are expected to vary widely in the character and concentration of complexing agents present. This information would be difficult to handle in the generic context even if it were available.

In the absence of detailed information, a simple model system of six common organics was used to mimic performance of real systems. This kind of approach was used by Morel et al. (10) in modeling speciation reactions in sewage effluents. The six model compounds selected represent several key functional groups and a broad span of abilities to complex metals. Acetate, tartrate, glycine, salicylate, glutamate and phthalate were selected.

Table 4. Selected Solids List

Metal									
As	Ba	Cd	Cr	Pb	Hg	Ni	Se	Ag	Tl
Orpiment	Barite	Otavite	$FeCr_2O_4$	Clypyromorph	Hg(l)	Millerite	Se, hex. blk.	Ag_2Se	Tl_2S
Realgar	$Ba_3(AsO_4)_2$	CdSe	$MgCr_2O_4$	Hyxpyromorph	Cinnabar	NiSe	Se (A)	Acanthite	
$Ba_3(AsO_4)_2$	Witherite	Greenockite	Cr_2O_3	Plumbogummite	Metacinna-barite	$Ni(OH)_2$	Ferro-selite	Ag°	
			$Cr(OH)_3(A)$	$Pb_3(PO_4)_2$			Ag_2Se		
			$Cr(OH)_3(C)$	Clausthalite			CdSe		
				Galena			FeSe		
				Cerrusite			NiSe		
				Hydcerrusite			Tl_2Se		
				$Pb(OH)_2$					

Concentrations of each were set by apportioning the median groundwater organic carbon concentration determined from STORET data equally (molar basis) among the six compounds. The median organic carbon concentration was 7.2 mg/l. Final distributions of the six selected ligands were determined as follows.

Ligand	Mol. wt.	Mol. wt. due to carbon
acetate^{-1}	59.05	24.02
tartrate^{-2}	148.09	36.03
glycine^{-1}	74.07	24.02
salicylate^{-2}	136.12	84.07
glutamate^{-2}	145.13	60.05
phthalate^{-2}	164.13	96.08
mean value	121.10	54.05

mean fraction carbon = 0.45

$$\frac{7.2 \text{ mg/l carbon}}{0.45} = 16.0 \text{ mg/l} = 1.3 \times 10^{-4} \text{ mol/l equivalent total ligand conc.}$$

Individual ligands were each added at one-sixth this concentration (2.2×10^{-5} mol/l).

MINTEQ inputs (in mg/l) were:

Ligand	MINTEQ input (mg/l)
acetate^{-1}	1.3
tartrate^{-2}	3.2
glycine^{-1}	1.6
salicylate^{-2}	3.0
glutamate^{-2}	3.2
phthalate^{-2}	3.6

Stability constants used in incorporating these ligands into the MINTEQ data base were extracted from the compilations of Sillén and Martel (11), Sillén et al. (12). Data added to the MINTEQ data file are tabulated in Table 5. Data were not included for metals other than the waste metals under investigation. Possible competing reactions with background metals were intentionally ignored so that errors resulting from the generic ligand selections would be in the environmentally conservative direction. Competition from background metals would tend to reduce the amounts of waste metals brought into solution by the organic ligands.

Table 5. Stability Constants for Generic Complexes Group

Metal	Stability Constants ($\log_{10}$)					
	acetate	tartrate	glycine	salicylate	glutamate	phthalate
Ba	0.41	2.54	0.77	0.21	1.28	2.33
H	4.76	K_1 = 4.16 K_{12} = 2.52	K_1 = 9.78 K_{12} = 2.35	K_1 = 13.4 K_{12} = 3	K_1 = 9.95 K_{12} = 4.28	K_1 = 5.40 K_{12} = 3.14
Cd	1.70	3.9	K_1 = 4.80 K_1 = 4.03		K_1 = 4.78 K_1 = 2.78	2.5
Cr	K_1 = 1.80 K_2 = 2.92		K_1 = 8.4 K_2 = 6.4 K_3 = 5.7			K_1 = 5.52 K_2 = 4.48 K_3 = 2.48
Ag	K_1 = 0.73 K_2 = -0.09		K_1 = 3.51 K_2 = 3.38			
Pb	2.1	3.78	K_1 = 5.47 K_2 = 3.39			
Tl		1.39				
Hg			K_1 = 10.8 K_2 = 20.0			
Ni	1.12		K_1 = 6.18 K_2 = 4.96	K_1 = 6.95 K_2 = 4.8	K_1 = 5.90 K_2 = 4.44	2.1

4.3 Criteria for Omitting Treatment of Metal Sorption

It is significant that the advective-dispersion model is of the infinite-source, steady state type. Introducing sorption reactions results in retarding the rate of solute movement; thus allowing more time lapse to reach the down-gradient measurement point. For degradable solutes (typically, most organic pollutants), this also influences the concentration of pollutant that eventually reaches the test point. Metals are considered to be conservative, however, and degradation is not considered. Therefore, the only result of adding a metal sorption algorithm to the dispersion model would be to change the time pollutants would be expected to arrive at the test point, not the concentrations that arrive. Said differently, sorption processes might determine when the groundwaters at the measurement point would be impaired, but not whether they would be impaired. For this reason, sorption processes were not treated in the dispersion model (K_d was set to zero). Treating metal sorption as a speciation reaction in the MINTEQ model would have introduced an inconsistency in the decision rule methodology for metals versus organics.

5. CAUTIONS AND PROBLEM AREAS

5.1 Specific Nature of Speciation Processes

The very specific natures of metal speciation reactions dictate that the distributions of equilibrium species will be sensitive to specific combinations of input components. This would apply in both the intensive and extensive contexts and is particularly relevant to the selection of generic input specifications. If key components have been inadvertently left out of the speciation mixture, or if they have been poorly estimated, speciation results could be drastically misleading. This is a critical

issue in land disposal analysis because ratios of waste material components can vary dramatically with time.

In this context, the relative concentration ratios of the ten test metals (or other waste metals not considered here) are as important to the speciation results as the generic background component mixture. Several of the waste metals under consideration can exist as anionic species that can combine with other metals to form highly insoluble solid phases. In some cases, these solids provide the solubility controls expected to dominate system behavior.

In the other extreme, addition of a given metal may result in a competitive effect causing another metal to dissolve (as in competition for selenide or sulfide ions). The possibilities are infinite. In this work the only combinations investigated were the addition of individual metals at five input concentrations, and nine E_h/pH combinations and a single generic background mixture. "Worst cases" were determined from this frame of reference.

5.2 Kinetic Limitations

Equilibrium metal speciation models such as MINTEQ predict the most stable equilibrium regardless of possible kinetic constraints. If any of the reactions leading to the formation of a solubility controlling solid is seriously hindred kinetically, an error in the conclusions would result. In an effort to safeguard against this possibility in the absence of kinetically endowed speciation models, the list of solubility-controlling solids was reviewed by a panel of experts. Where questions arose regarding the kinetic feasibility for formation of a given solid, that solid was eliminated (presumed not to form). In this way, errors due to the lack of

adequate kinetic information were in the conservative direction.

5.3 Imperfections in the Data Base

All speciation models rely on a wide range of data from many sources. The MINTEQ data base has been carefully assembled over time and can be considered state-of-the-art. It is, however, still subject to many limitations reflecting our imperfect understanding of the very complex chemistries involved. The recently added data on reactions for chromium, mercury, selenium, and thallium have not yet undergone thorough critical review over time even though every effort was made to assemble the best available data.

6. RESULTS

6.1 Reporting Format

Speciation modeling results for each metal consist of a series of graphs showing total dissolved phase metal concentrations (after speciation) resulting from various total metal input concentrations. A total of five input concentrations were investigated which corresponded to the following multiples of the current DWS for each metal.

1) DWS + background
2) 25 times DWS
3) 50 times DWS
4) 100 times DWS
5) 10,000 times DWS

Two graphs are provided for each metal in the Appendix. The first of these covers only input concentrations 1 through 4 above. The second graph in each set covers the entire range up to 10,000 times DWS input level, but does not give usable definition at lower concentrations because of the large large scale.

Total dissolved metal concentrations for each metal at each input level are summarized in Table 6. Table 7 lists the solids responsible for controlling solubilities where metal concentrations after speciation were less than input concentrations.

Dissolved phase concentrations of only four metals were significantly limited by the formation of solid phases. These metals were classified as "reltively immobile." The other six test metals were almost completely dissolved under the worst case conditions tested and were classified as "mobile."

Relatively immobile metals	Mobile metals
chromium	arsenic
mercury	barium
selenium	cadmium
silver	lead
	nickel
	thallium

Additional work was performed on the immobile metals to determine their sensitivities to E_h conditions outside the initial uncertainty window. Since all four immobile metals were controlled by solids containing reduced components (low oxidation states), only the E_h range above the upper uncertainty window limit of 106 mv was investigated further. Total dissolved phase concentrations (at the worst-case pH values) were determined as a function of increasing E_h up to the point of total dissolution. Results of these studies are reported in Sections 6.3.1 - 6.3.4.

Table 6. Worst Case MINTEQ Output Concentrations Compared to Total Metal Input Concentrations (mg/l)

	pH, Eh mv	DWS + back Input/ /Output	25 DWS Input/ /Output	50 DWS Input/ /Output	100 DWS Input/ /Output	10,000 DWS Input/ /Output
Arsenic	8.1, 106	0.060	1.25	2.50	5.00	500
		$3.58X10^{-7}$	1.18	2.43	4.93	500
Barium	6.8, -206	1.70	37.5	75.0	150	15,000
		1.70	37.5	75.0	150	13,967
Cadmium	6.8, 106	0.010	0.125	0.250	0.500	50.0
		0.010	0.120	0.250	0.500	50.0
Chromium	5.5, 106	0.140	3.00	6.00	12.00	1,200.0
		0.00513	0.079	0.079	0.079	0.079
Lead	5.5, 106	0.030	0.500	1.00	2.00	200
		$1.25X10^{-6}$	0.398	0.887	1.67	199.7
Mercury	8.1, 106	0.0035	0.0750	0.1500	0.300	30.0
		0.0018	0.0243	0.0243	0.0243	0.0243
Nickel	5.5, 106	0.160	3.750	7.500	15.00	1,500
		0.160	3.748	7.497	14.97	1,500
Selenium	8.1, 106	0.050	1.13	2.25	4.50	450
		0.046	0.0808	0.0808	0.0808	0.0805
Silver	6.8, -206 (Undeterminant)	0.100	2.25	4.50	9.00	900
		$\approx 9X10^{-7}$	$\approx 9X10^{-7}$	$\approx 9X10^{-7}$	$\approx 9X10^{-7}$	$\approx 9X10^{-7}$
Thallium	6.8, -206	0.059	0.480	0.960	1.92	192
		0.059	0.480	0.950	1.29	81.3

Table 7. Solubility Controlling Solids (Worst Case Conditions)

Metal / Input Conc.	DWS plus background	25 X DWS	50 X DWS	100 X DWS	10,000 X DWS
Arsenic	$Ba_3(AsO_4)_2$	$Ba_3(AsO_4)_2$	$Ba_3(AsO_4)_2$	$Ba_3(AsO_4)_2$	$Ba_3(AsO_4)_2$
Barium	None	None	None	None	Barite
Cadmium	None	CdSe	CdSe	CdSe	CdSe, Otavite
Chromium	$FeCr_2O_4$	$FeCr_2O_4$ Cr_wO_3	$FeCr_2O_4$ Cr_2O_3	$FeCr_2O_4$ Cr_2O_3	$FeCr_2O_4$ Cr_2O_3
Lead	Plumbogummite	Plumbogummite Clausthalite	Plumbogammite Clausthalite	Clausthalite Clpyromorph	Clpyromorph
Mercury	None	Hg(l)	Hg(l)	Hg(l)	Hg(l)
Nickel	None	NiSe	NiSe	NiSe	NiSe
Selenium	Ag_2Se	Ag_2Se Se, hex. black	Ag_2Se Se, hex. black	Ag_2Se Se, hex. black	Ag_2Se Se, hex. black
Silver	Acanthite	Acanthite	Acanthite	Acanthite	Acanthite
Thallium	None	None	None	None	Tl_2S

Note: Some of the solids listed did not give effective solubility control because the quantity of sister anionic component available was limiting at high input concentrations of the test metal.

6.2 Interpretations/Recommendations for the Mobile Metals Group

6.2.1 Arsenic

The worst case conditions were at high E_h (106 mv) and high pH (8.1) where the arsenic (V) species were dominant over dissolved arsenic (III) species by several orders of magnitude. Sums of solution species in the V and III oxidation states were, respectively, 4.78×10^{-12} and 4.97×10^{-19} mol/l (3.58×10^{-7} and 3.73×10^{-17} mg/l). Predominant solution species were $H_2AsO_4^-$ (3.6%) and $HAsO_4^{2-}$ (96.3%). The controlling solid was $Ba_3(AsO_4)_2$, which accounted for 8.00×10^{-7} mol/l (3.00×10^{-2} mg/l) or nearly all of the total system arsenic input (at the lowest concentration). As arsenic input concentrations increased through the range, the quantity of $Ba_3(AsO_4)_2$ precipitated increased until the background barium source concentration became limiting. This occurred at the 25 X DWS arsenic input level. After that, additional arsenic additions remained in solution and the output concentration increased linearly up to 10,000 X DWS input levels (500 mg/l).

Arsenic levels would be strongly attenuated to higher input levels in systems where barium ion was present in adequate supply. It would, however, not represent a conservative view to assume this to be the case. Some groundwaters would contain even less barium than the median values used.

Recommendation: The median background concentration of dissolved barium was 0.200 mg/l. Based on the composition of $Ba_3(AsO_4)_2$, this would be sufficient to strongly limit dissolved arsenic levels up to input concentrations of about 0.073 mg/l. Further arsenic additions would remain in solution. Assuming a dilution factor of 22 due to dispersion

and an allowable concentration of 0.05 mg/l at the drinking water source, 22 X 0.05 = 1.10 mg/l would be the allowable leachate input concentration if no solids precipitated. Adding to this the 0.073 mg/l of arsenic expected to precipitate as $Ba_3(AsO_4)_2$, the maximum allowable leachate concentration would be about 1.08 mg/l.

6.2.2 Barium

The worst case conditions were at low E_h (-206 mv) and pH = 6.8. Because of the low E_h, $Ba_3(AsO_4)_2$ precipitation was not a factor. Similarly, the solubility product for barite was not exceeded for input levels up to more than 100 times the DWS. Barite did precipitate at an input level of 10,000 times the DWS. The only significant solution species was the barium (II) ion. The input/out graph reflected a linear 1:1 relationship up through 100 times the DWS input concentration.

Recommendation: For a dilution factor of 22 due to dispersion and DWS = 1.50 mg/l, the allowable leachate concentration would be 1.50 X 22 = 33.0 mg/l.

6.2.3 Cadmium

The worst case conditions were at pH 6.8 and high E_h (106 mv). Under these conditions, traces of CdSe precipitated at inputs above 25 times DWS, but the quantities of CdSe were limited by the quantity of selenium available. A very small amount of Otavite also precipitated at the 10,000 times DWS input level. Only negligible changes in solution phase cadmium concentrations resulted from either solid.

Recommendation: For a dilution factor of 22 due to dispersion and DWS = 0.005 mg/l, the allowable leachate concentration would be approximately 0.005 X 22 = 0.11 mg/l because only insignificant quantities of solids are expected to precipitate.

6.2.4 Lead

The worst case conditions for lead were at low pH (5.5) and high E_h (106 mv). The predominant solution species was Pb (II) ion (73%) with minor contributions from $PbHCO_3^+$, $PbSO_4$ (aq), $PbCO_3$ (aq) and a complex with tartrate. Plumbogummite, clausthalite and clypyromorph precipitated at various points along the nonlinear input/output curve. Dissolved lead concentrations were somewhat reduced due to precipitation over the whole range, but the effect was not significant at the highest input concentrations. Formation of solids was limited by the availability of the anionic components in the solid.

Recommendation: Assuming a dilution factor of 22 due to dispersion and DWS = 0.020 mg/l, the allowable output concentration would be 22 X 0.020 = 0.440 mg/l. This limit would be exceeded at input concentrations slightly above the 25 times DWS input concentration. In this range about 20 percent of the added lead precipitated. Because the associated anionic components became limiting at very high lead input concentrations, precipitation did not significantly influence dissolved lead concentrations at the higher input levels. At the 10,000 times DWS linput, concentration virtually all the added lead remained in solution.

6.2.5 Nickel

The worst case conditions for nickel were pH 5.5 and E_h of 106 mv. The predominant solution species was Ni^{2+} ion. The only solid which

precipitated was NiSe and it did not control nickel concentrations at high loadings because the source of selenium was limiting.

Recommendation: Assuming a dilution factor of 22 and the DWS = 0.15 mg/l, the allowable MINTEQ output concentration would be 22 X 0.15 = 3.30 mg/l. Since virtually all the added nickel was in the dissolved phase, this output concentration would be exceeded at input concentrations greater than 22 times the DWS.

6.2.6 Thallium

The worst case conditions for thallium were found for pH = 6.8 and E_h = -206 mv. The predominant solution species was Tl^{+1} ion and no solids formed until input concentrations reached the 10,000 times DWS level, where Tl_2S precipitated.

Recommendation: Assuming a dilution factor due to dispersion of 22 and the DWS = 0.019 mg/l, the allowable output concentration would be 0.019 X 22 = 0.42 mg/l. Since no thallium precipitated up to this level, 0.42 mg/l would also be the allowable leachate concentration.

6.3 Interpretations/Recommendations for the Relatively Immobile Metals Group

6.3.1 Chromium

The worst case conditions for chromium were at low pH (5.5) and high E_h (106 mv). The predominant solution species were $Cr(OH)^{2+}$ (61%), a complex with phthalate (22%), Cr^{3+} (7%), $Cr(OH)_2^+$ (7%), and complex with glycine (2%). Two solids ($FeCr_2O_4$ and Cr_2O_3) were predicted in the initial model runs. Ferrous chromite is thermodynamically stable, but not likely to form in low temperature groundwater environments. Results of repeated model runs with $FeCr_2O_4$ removed from consideration are illustrated in Figure 4.

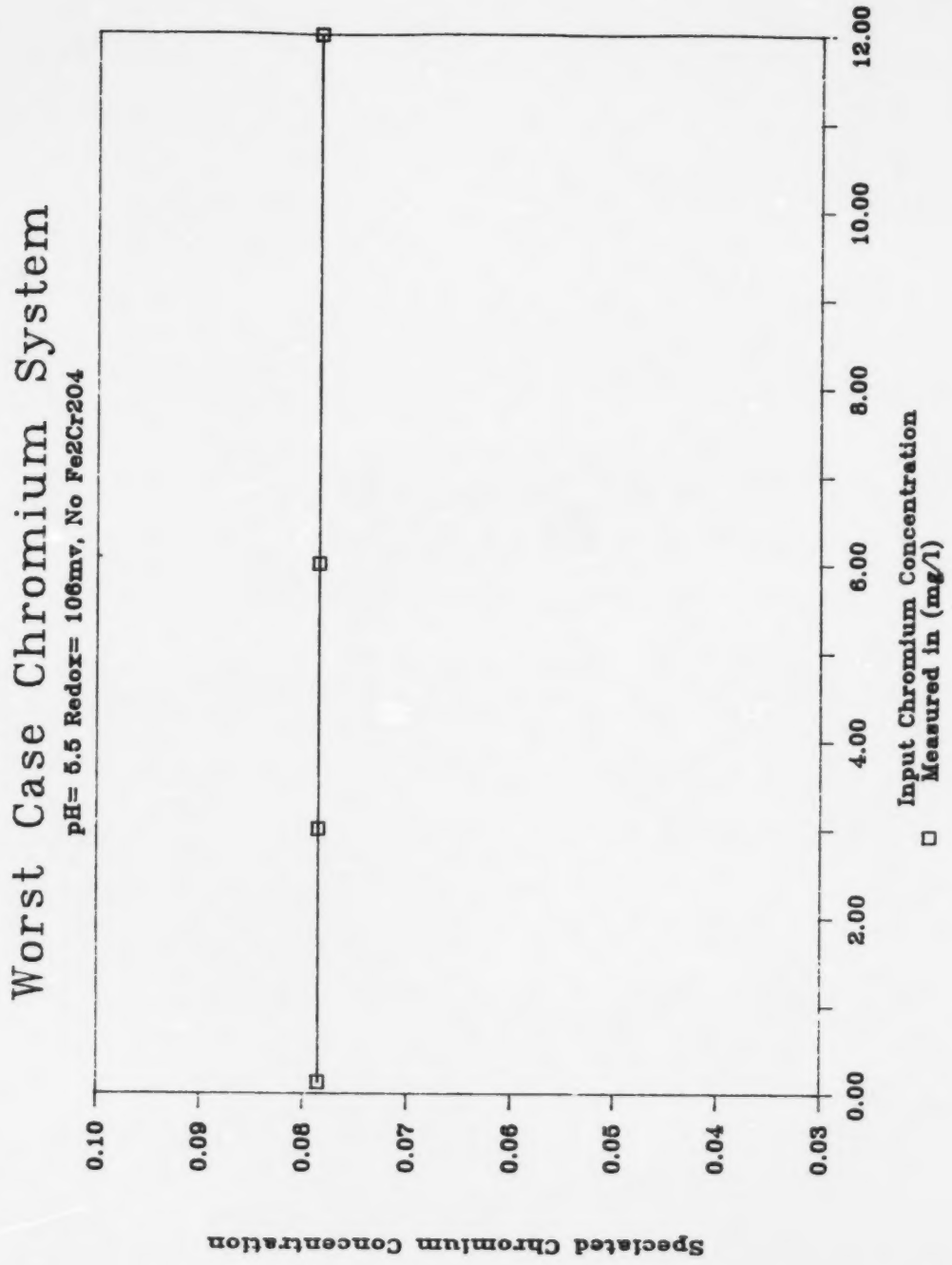


Figure 4. MINTEQ results for chromium with the ferrous chomite ($FeCr_2O_4$) solid removed.

With $FeCr_2O_4$ removed only Cr_2O_3 precipitated. This solid limited dissolved chromium concentrations to 0.0785 mg/l, which is slightly below the proposed DWS of 0.12 mg/l even without considering dilution due to dispersion.

The worst case conditions for chromium occurred at the maximum E_h (+106 mv) defined by the uncertainty window. Since the controlling solid involved Cr(III), the possibility of higher dissolved chromium levels under more oxic conditions was considered. Figure 5 illustrates results of model runs performed as a function of E_h at an input concentration of 25 times the DWS and at the worst case pH of 5.5. The concentration plateau caused by precipitation of Cr_2O_3 persisted to E_h levels of at least 500 mv. This is well above the expected values for groundwaters. The more soluble Cr(VI) species were predominant at higher E_h levels.

It should be noted that MINTEQ is an equilibrium model. It does not address possible kinetic limitations on the Cr(VI) to Cr(III) conversion. If chromium wastes were introduced as Cr(VI) species and the conversions to Cr(III) were sufficiently slow, Cr_2O_3 would not precipitate. Assuming a flow velocity of 1.0 m/day and a longitudinal distance (to the point of exposure) of 150 m, the total time for reaction would be 150 days. The conversion of Cr(VI) to Cr(III) and the subsequent precipitation of Cr(III) as Cr_2O_3 would both have to approach completion in this time period to effectively limit dissolved chromium concentrations. The most likely limitation would be the reduction of Cr(VI).

Recommendation: In the absence of kinetic limitations, dissolved chromium concentrations are expected to be limited to about 0.08 mg/l due to precipitation of Cr_2O_3. Assuming a dilution factor of 22 due to dispersion, the chromium concentration expected at the point of exposure would be below the DWS.

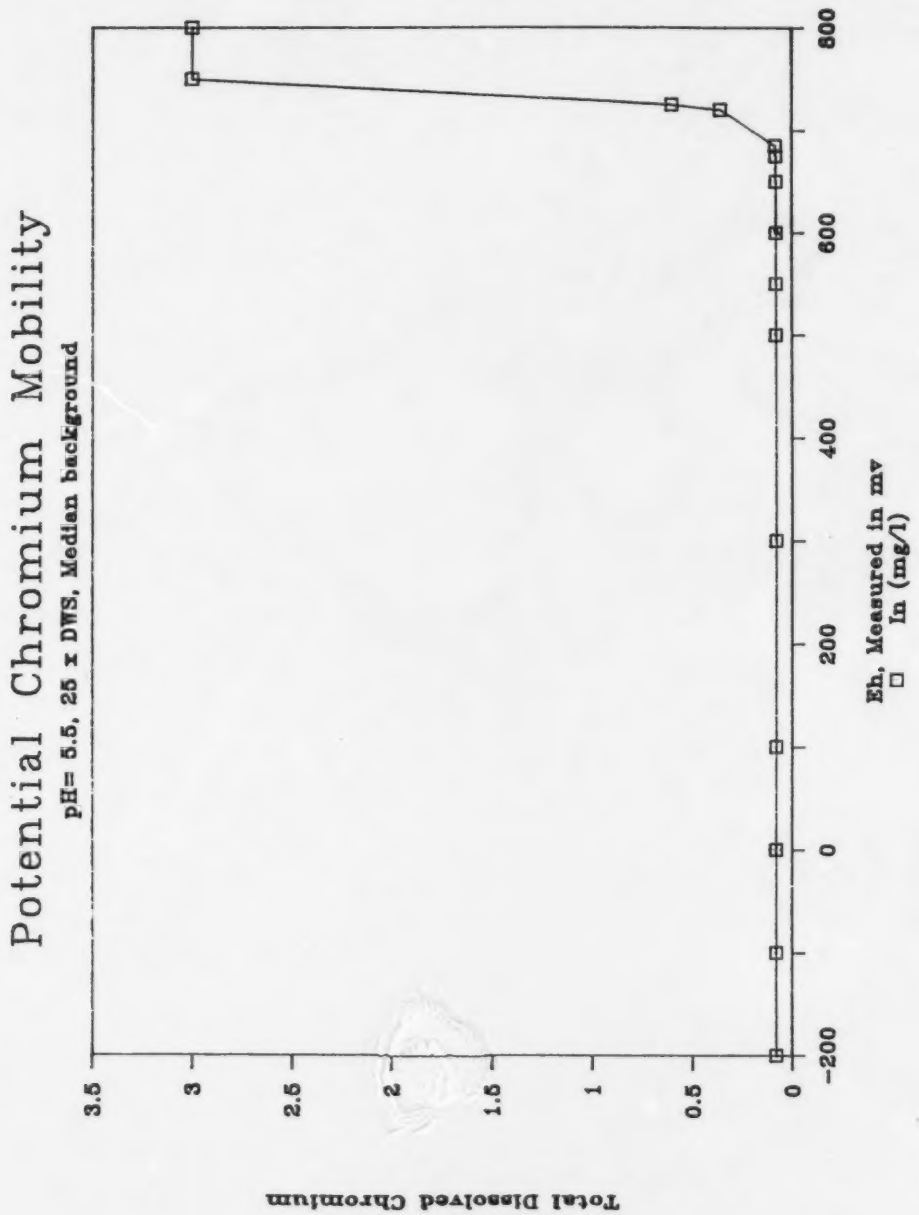


Figure 5. Sensitivity of dissolved chromium concentration to E_h at pH = 5.5.

6.3.2 Mercury

The worst case conditions for mercury were high pH (8.1) and high E_h (106 mv), and the predominant solution species was Hg° (aq). The controlling "solid" was Hg°(l) which limited dissolved concentrations to about 0.024 mg/l. This concentration plateau would be expected to continue until the E_h/pH buffering capacity of the system was exceeded.

It should be noted that mercury would be more soluble in more oxidizing environments due to the formation of Hg(II) ion. Figure 6 illustrates the increased solubility of mercury with increasing E_h. Above 500 mv the added mercury was totally dissolved at input concentrations of 25 times DWS. Increased solubility would also result if organomercury compounds formed. These were not treated in the MINTEQ data base.

Recommendation: Assuming the E_h/pH buffering capacity of the groundwater matrix is not exceeded, mercury is expected to precipitate as Hg°(l) at E_h = 106 mv. This would limit down-gradient mercury concentrations to about 1/22 X 0.0243 = 0.0011 mg/l assuming a dilution factor of 22 due to dispersion. The transition to Hg(II) as the predominant species occurs over the E_h range 300 to 500mv at pH 8.1. Above 500 mv the down-gradient concentrations would exceed the DWS for input concentrations greater than 22 times DWS. Only one E_h value above 500 mv was observed in the STORET data search.

6.3.3 Selenium

The worst case conditions were at high pH and high E_h. Under these conditions SeO_3^{-2} (88%) and $HSeO_3^{-1}$ (12%) were the predominant solution species. The maximum E_h investigated in the uncertainty window was 106 mv and this was the worst case E_h. It should, however, be noted that

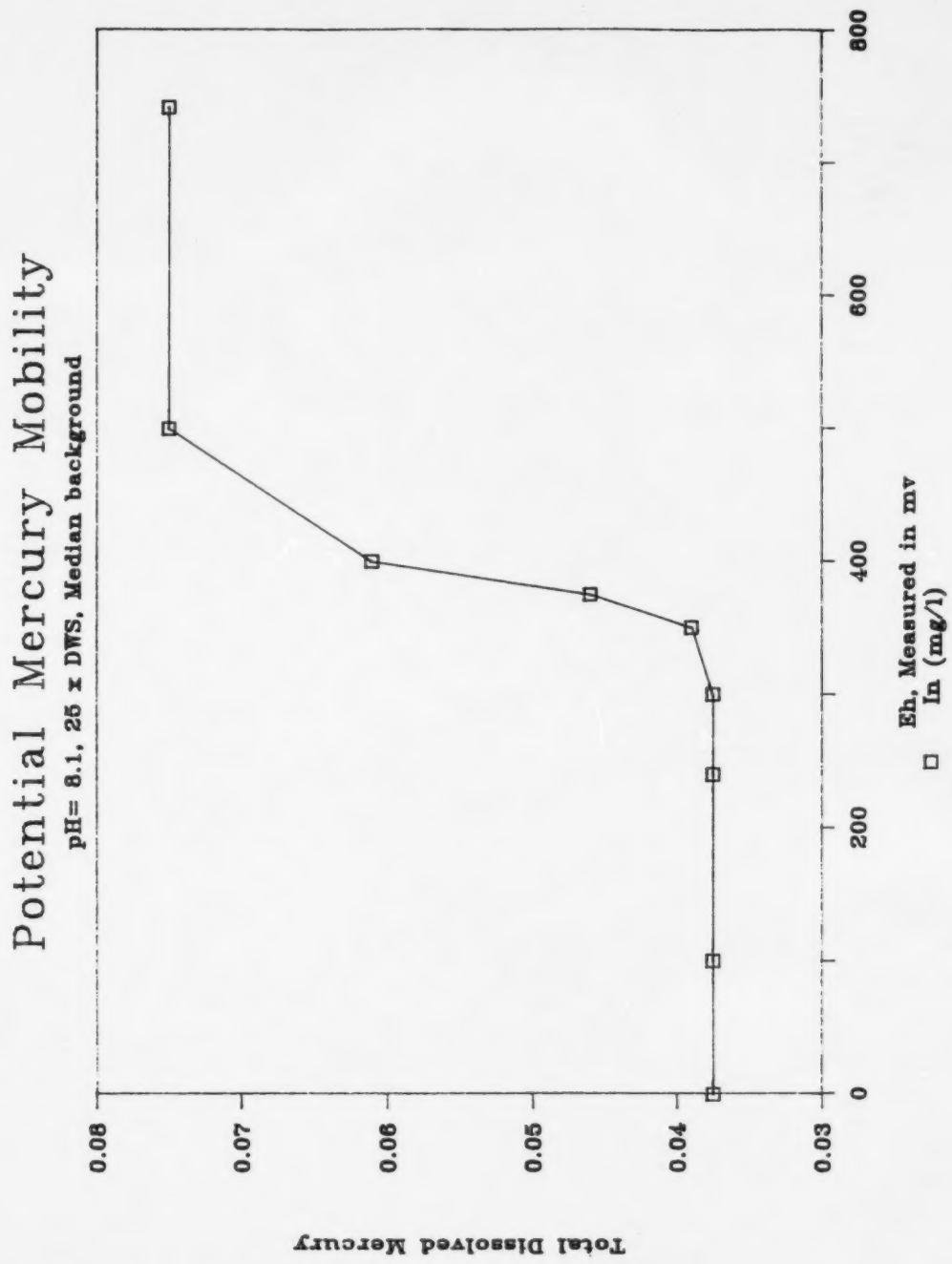


Figure 6. Sensitivity of dissolved mercury concentration to E_h at pH = 8.1.

further increases in E_h (more oxidizing conditions) would tend to oxidize selenium to the Se (VI) oxidation state. This would reduce the quantities of selenium in the (-II), (0) and (IV) states and tend to minimize the potential for precipitation of highly insoluble metal selenides such as Ag_2Se as well as elemental selenium. In conbination with high pH (8.1) the resulting dominant solution species would be the relatively soluble SeO_4^{2-} ion. At E_h levels of 300 - 500 mv and neutral pH's, selenium would dissolve totally up to reasonably high input levels. Figure 7 shows the sensitivity of total dissolved selenium (at 25 times DWS input level) as a function of E_h at pH = 8.1.

Based on a maximum E_h of 106 mv, as defined by the uncertainty window, the controlling solids were Ag_2Se and the elemental allotrope Se°, hexagonal black. Since the hexagonal black allotrope is not expected to form at temperatures of 14°C, it was removed from consideration and the model runs repeated. Amorphous Se precipitated in the repeat runs (Figure 8). It was only about three times more soluble than the hexagonal black allotrope.

Recommendation: Selenium solubility is very sensitive to E_h. Dissolved concentrations were limited to 0.34 mg/l at E_h = 106 mv. Assuming a dilution factor of 22 due to dispersion, concentrations at the down-gradient exposure point would not exceed 0.015 mg/l. At higher E_h's, the more soluble Se(IV) and Se(VI) species dominate and selenium dissolves completely up to levels which would easily exceed the DWS at the down-gradient exposure point after allowing for a dilution factor of 22.

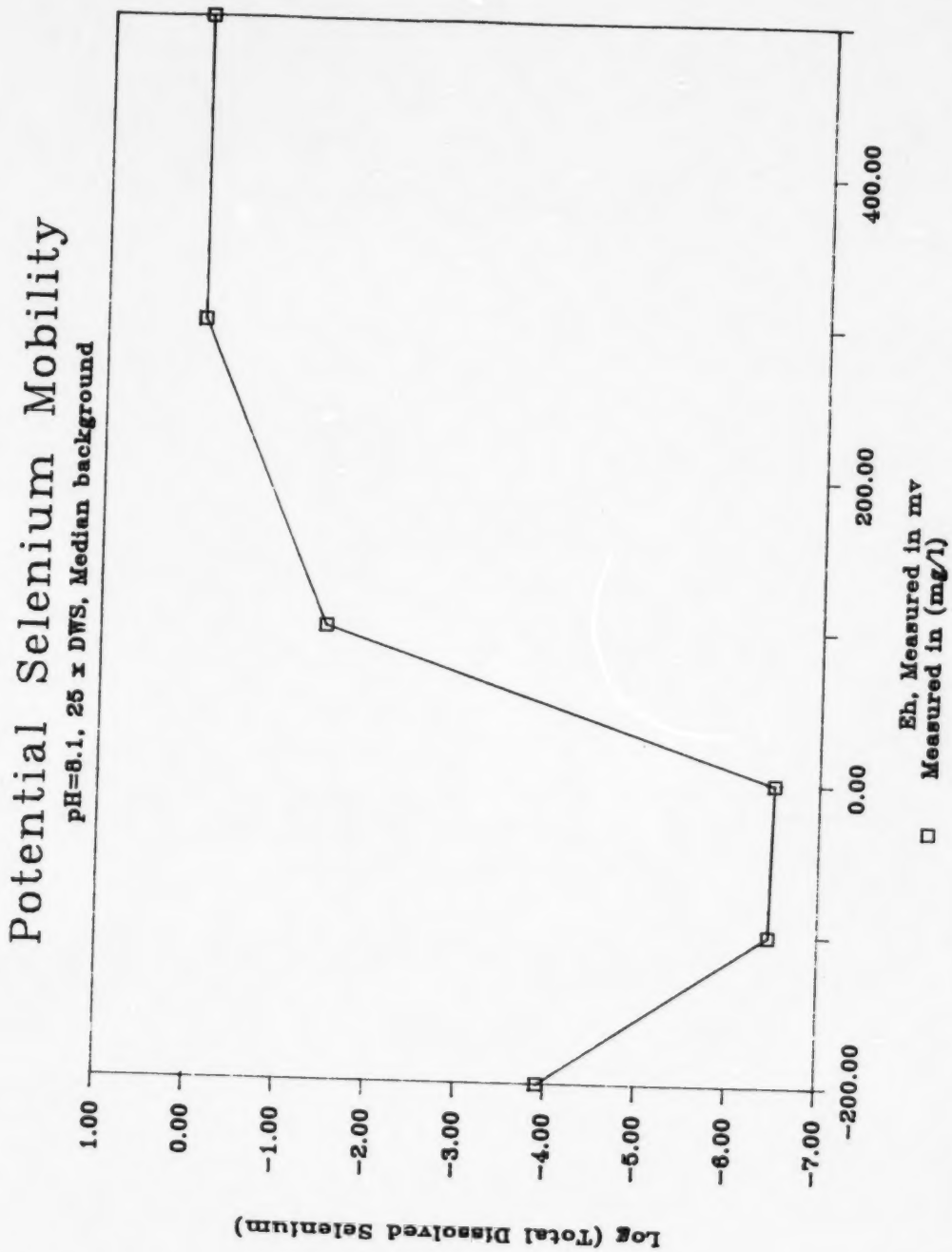


Figure 7. Sensitivity of dissolved selenium concentration to E_h at pH = 8.1.

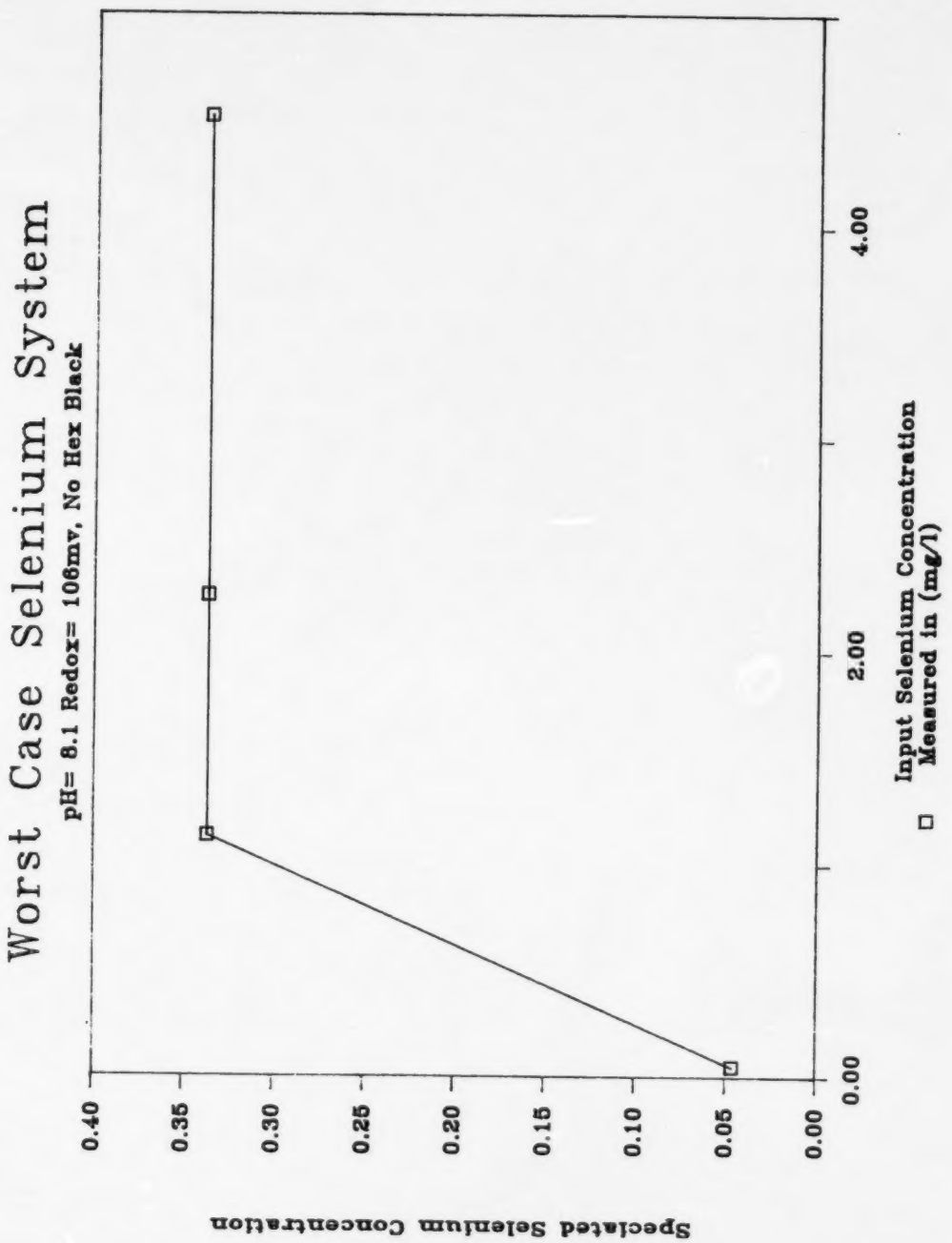


Figure 8. MINTEQ results for selenium with the selenium hexogonal black solid removed.

6.3.4 Silver

Worst case conditions for silver could not be determined with certainty because nearly all the system silver precipitated, leaving such small solution concentrations that numeric underrun problems developed with the computer. Dissolved silver concentrations were below decimal precesion which could be tracked with certainty in all E_h, pH combinations investigated. The Ag_2S solid (acanthite) with a solubility product (K_{sp}) of about 6.2×10^{-52} (13) illustrates the problem. For relatively reduced systems where even a trace source of sulfide ion exists, silver precipitates as Ag_2S to the point that dissolved concentrations are below the decimal precision available in making reliable mass balance calculations. At the 100 DWS silver input level (8.34×10^{-5} mol/l) a solution equivalent concentration of 8.34×10^{-5} mol/l of Ag_2S solid formed at pH 6.8 and E_h = -206 mv. Raising the E_h to 106 mv (highest level investigated) would reduce sulfide ion availability many orders of magnitude. Bisulfide (HS^-) ion concentrations on the order of 10^{-29} mol/l would be expected at E_h = 106 mv. Even so, silver ion concentrations would be very low.

$$Ksp = [Ag^+]^2 \, [10^{-29}] = 6.2 \times 10^{-52}$$

$$[Ag^+] \approx \left(\frac{10^{-51.2}}{10^{-29}}\right)^{1/2} \approx 8 \times 10^{-12} \text{ mol/l}$$

which corresponds to 8.6×10^{-7} mg/l.

Recommendation: Using the above estimate and a dilution factor of 22 due to dispersion, the maximum dissolved silver concentration expected at the down gradient measurement point would be approximately

$$\frac{8.6 \times 10^{-7}}{22} = 3.9 \times 10^{-8} \text{ mg/l} \qquad (23)$$

which is far below the DWS. Silver is not expected to migrate unless substantial conncentration of ammonia or cyanide ion are present. If either is present, more soluble complexes would be expected. Ammonia and cyanide ion were not included in the present MINTEQ data base.

7. References

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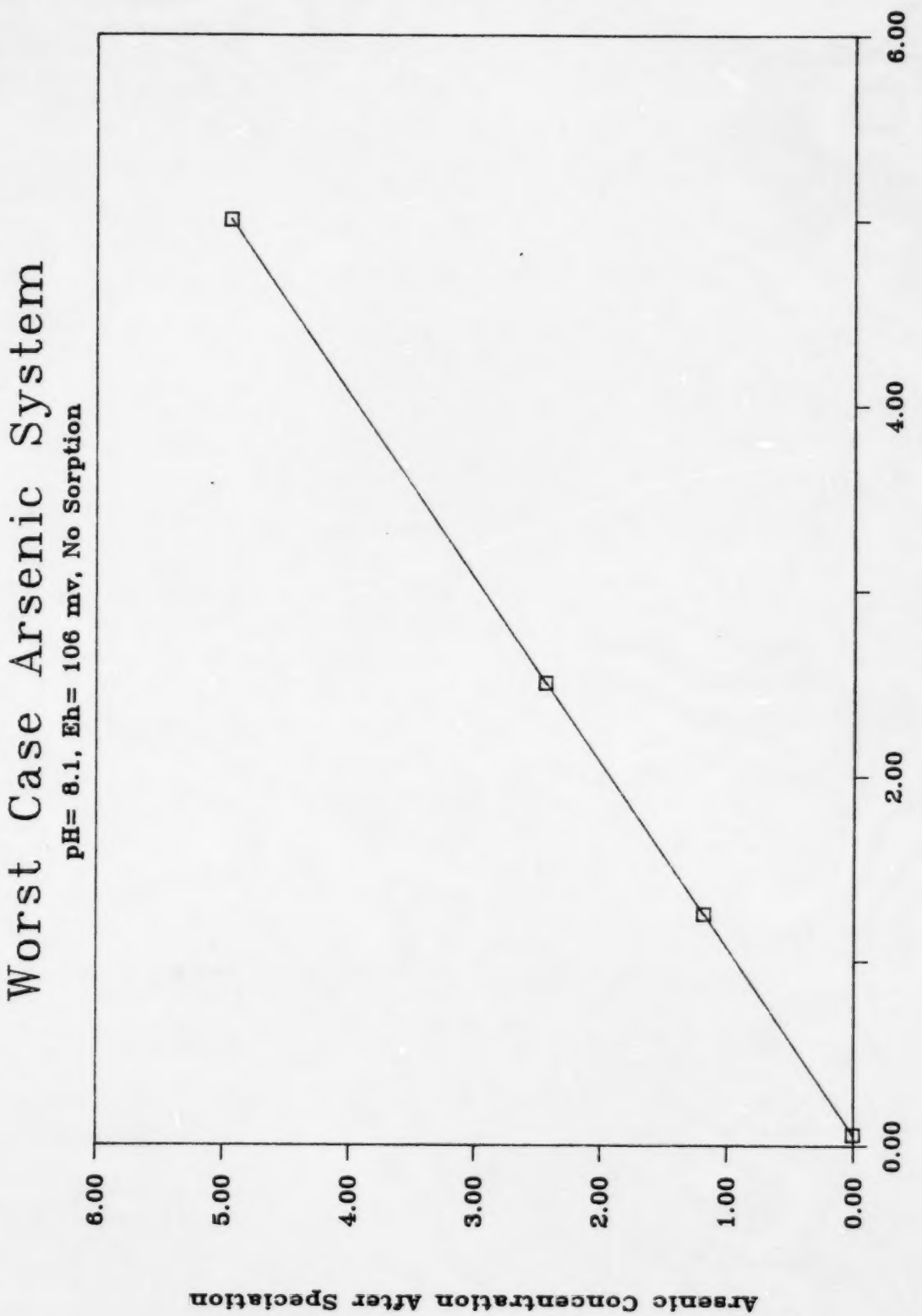
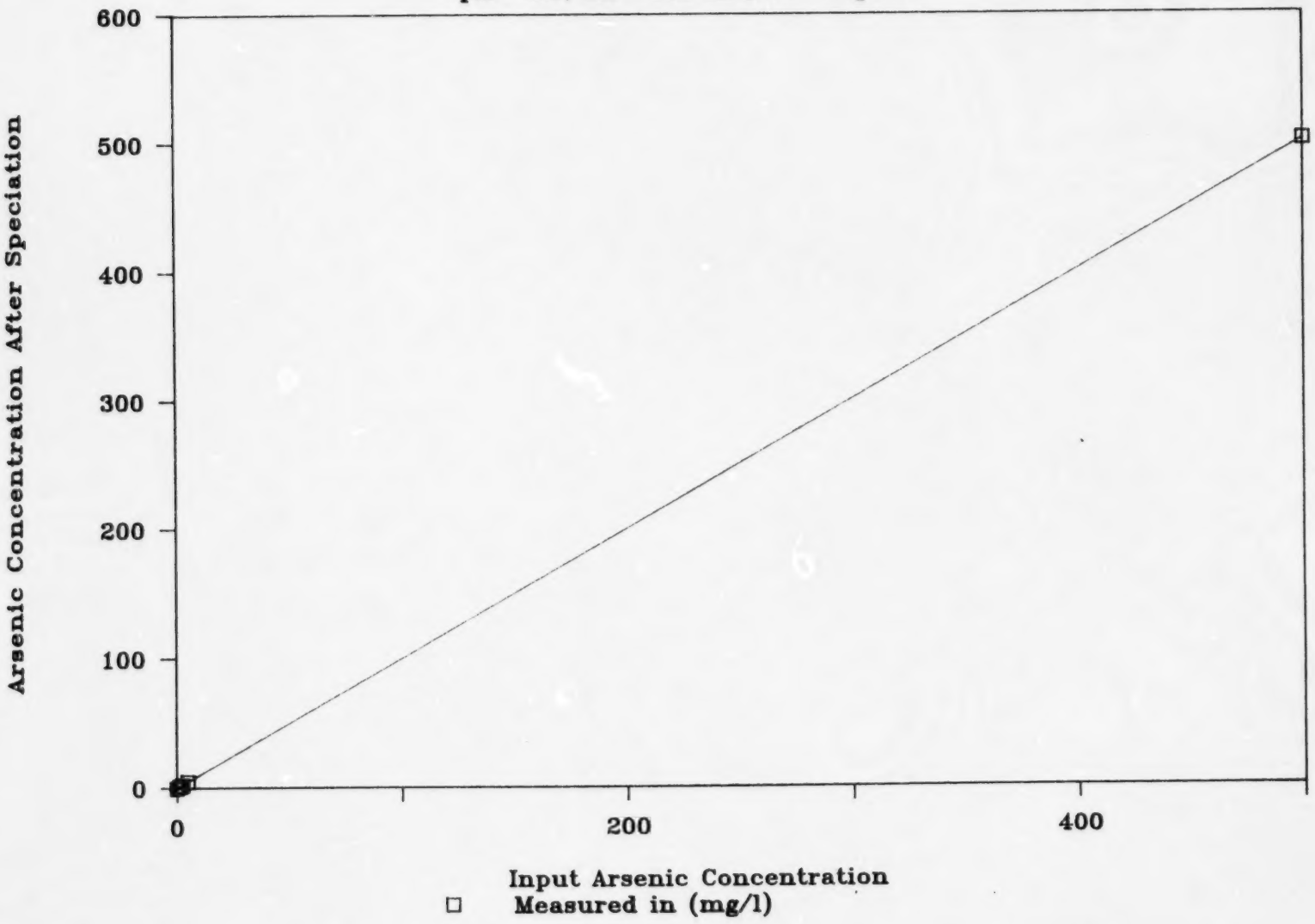

Worst Case Arsenic System
pH= 8.1, Eh= 106 mv, No Sorption
Arsenic Concentration After Speciation
0.00
1.00
2.00
3.00
4.00
5.00
6.00
0.00
2.00
4.00
6.00
Input Arsenic Concentration
Measured in (mg/l)

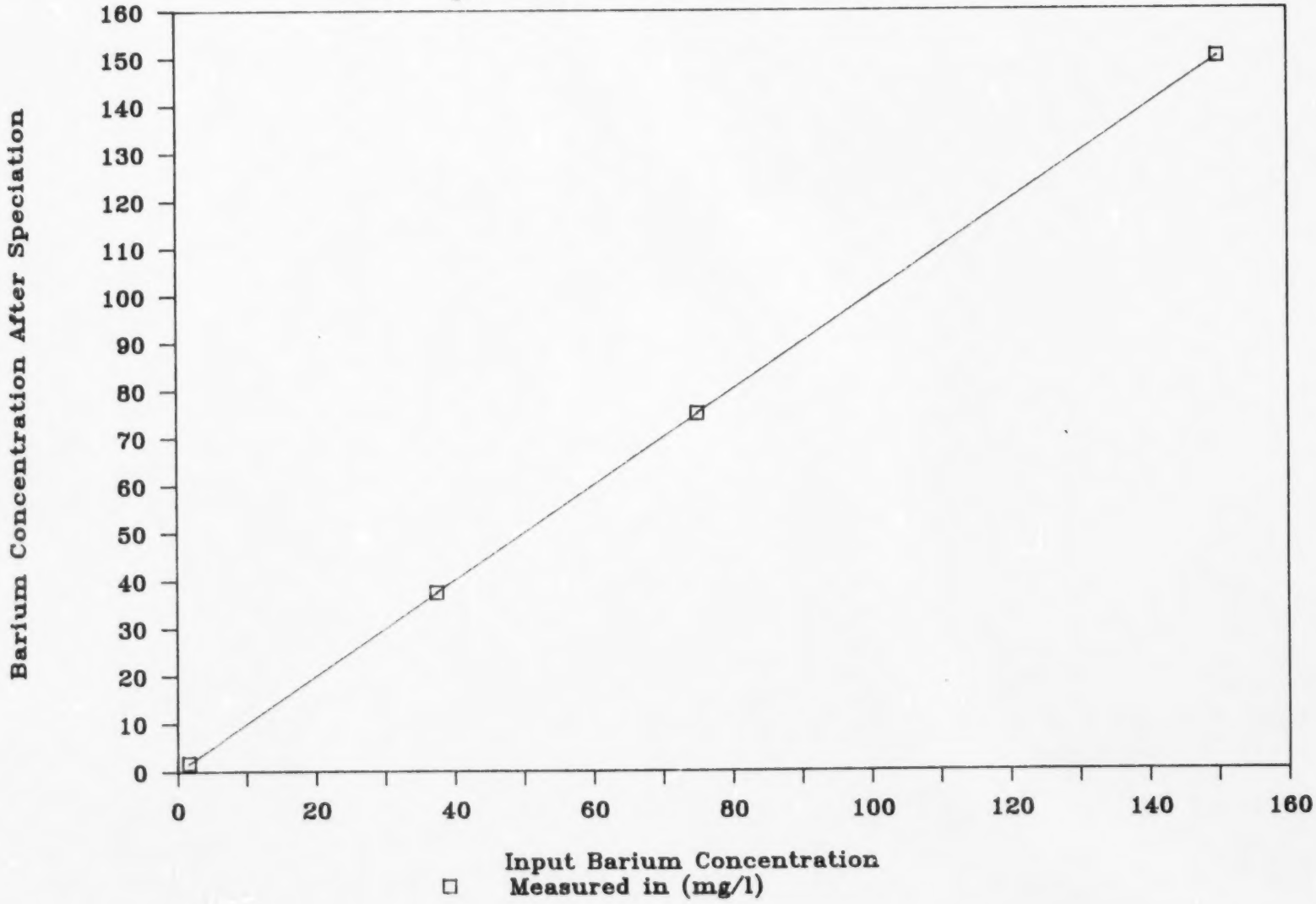
Worst Case Arsenic System

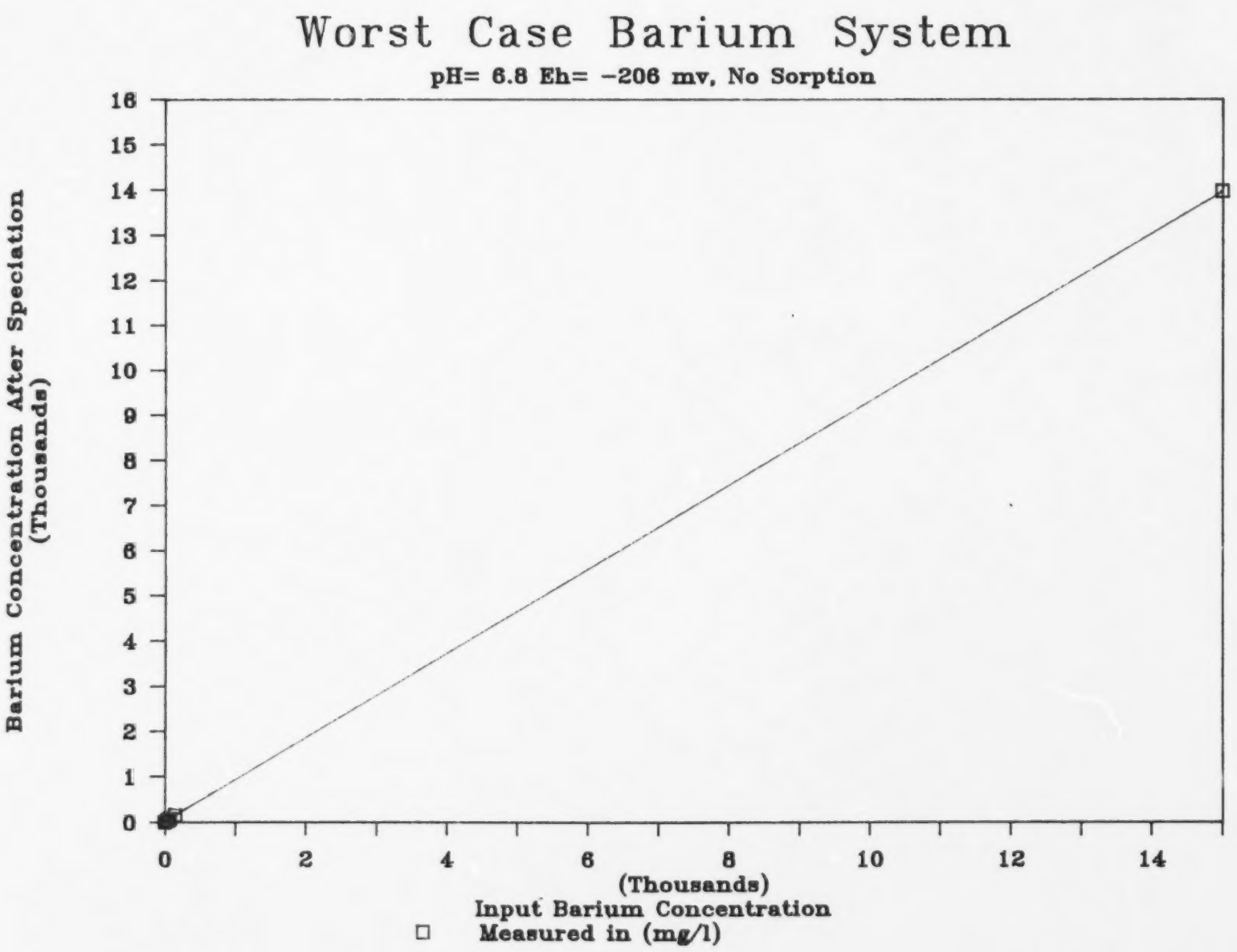
pH= 8.1, Eh= 106 mv, No Sorption

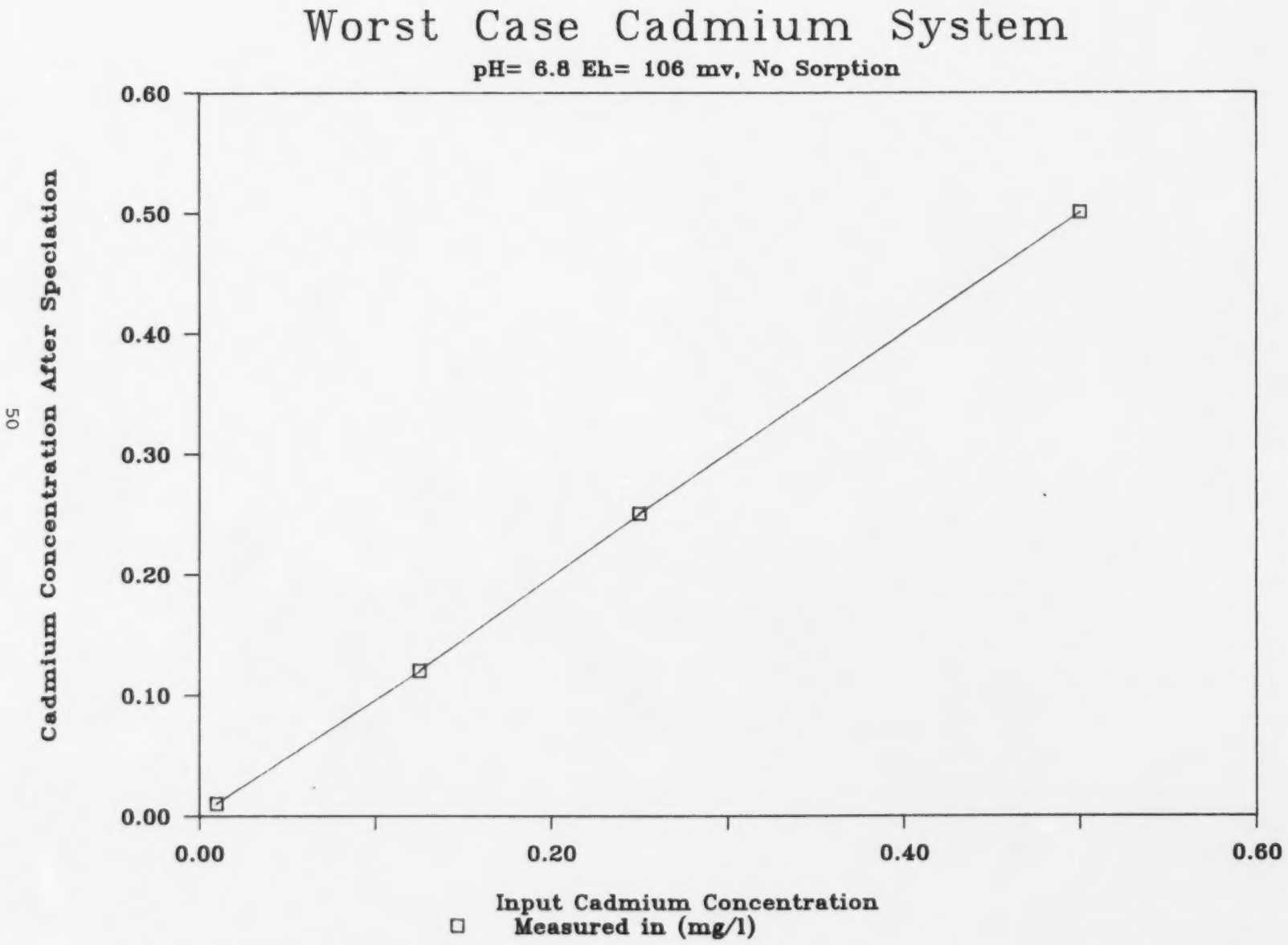


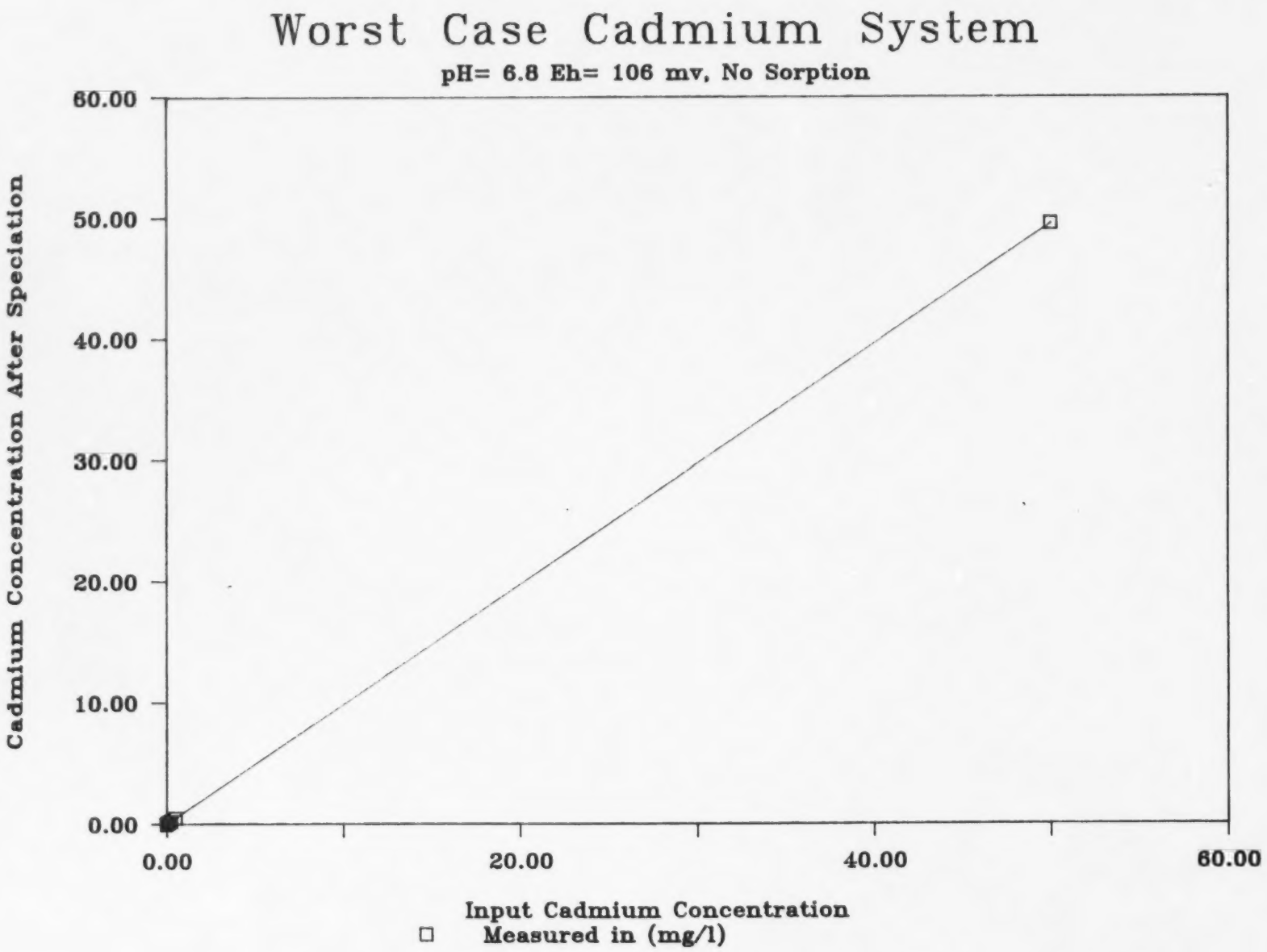
Worst Case Barium System

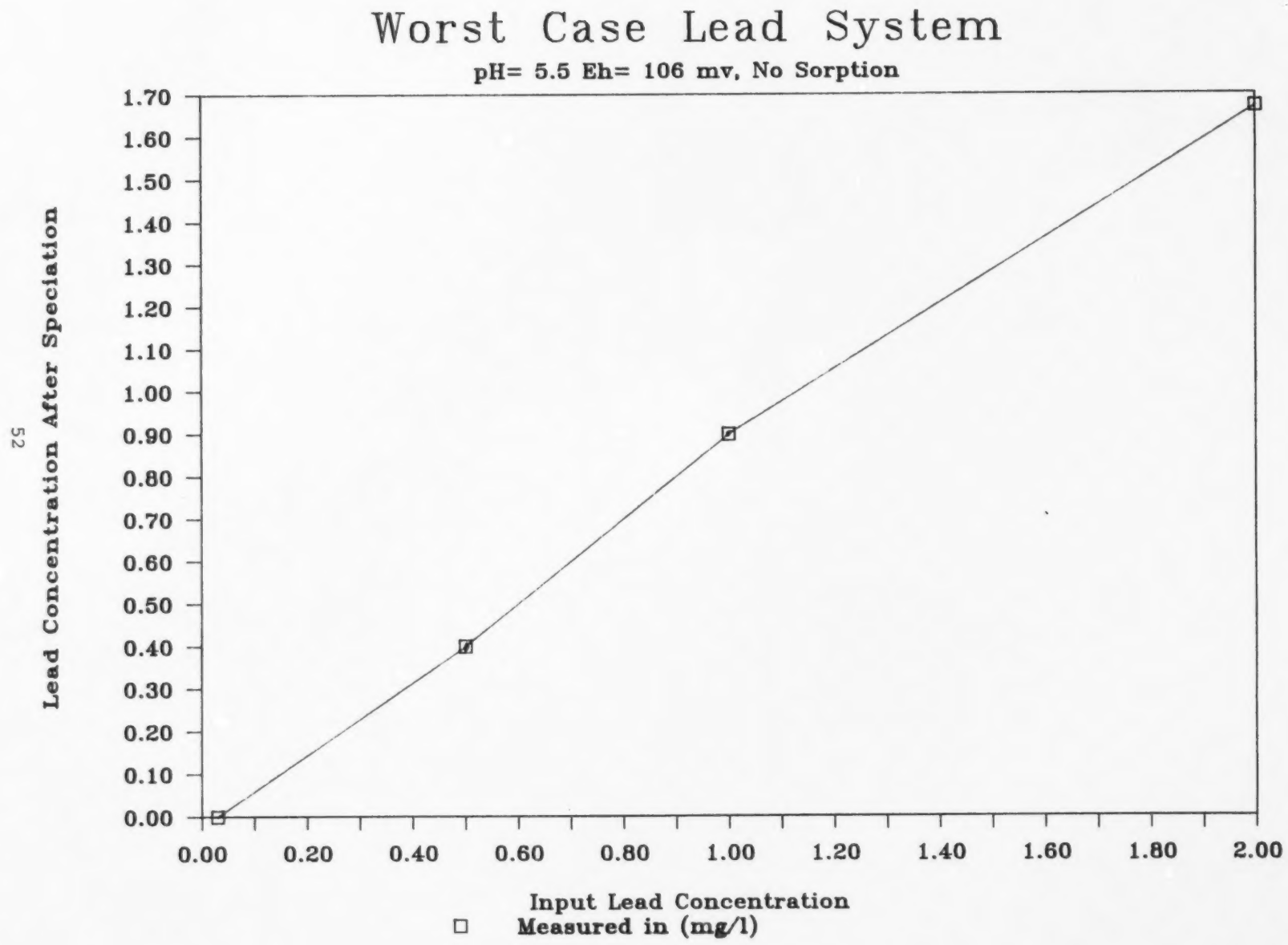
pH= 6.8 Eh= -206 mv, No Sorption

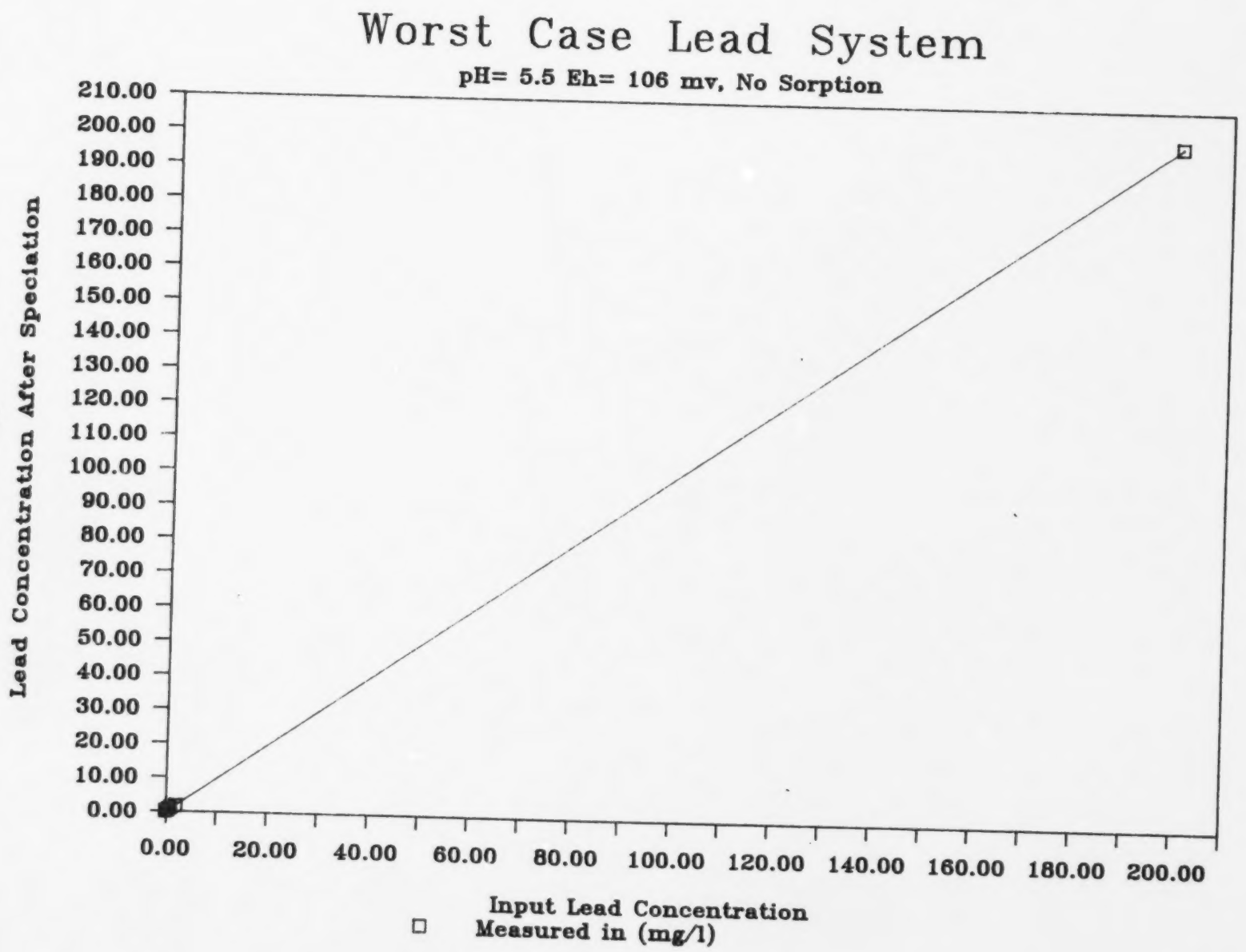



Worst Case Barium System
pH= 6.8 Eh= -206 mv, No Sorption
Barium Concentration After Speciation
(Thousands)
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
0
2
4
6
8
10
12
14
(Thousands)
Input Barium Concentration
Measured in (mg/l)

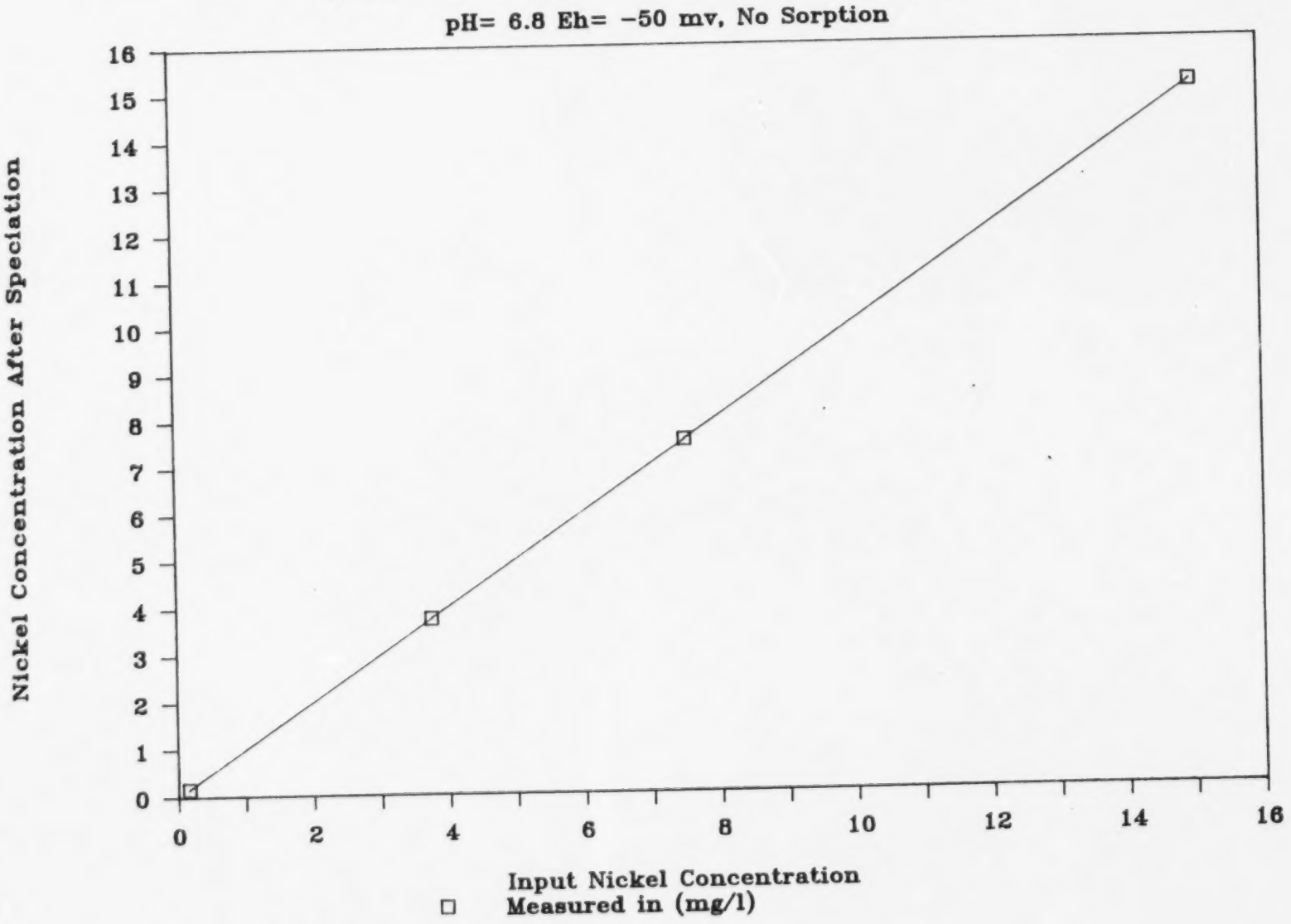

Worst Case Cadmium System
pH= 6.8 Eh= 106 mv, No Sorption
Cadmium Concentration After Speciation
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0.00
0.20
0.40
0.60
Input Cadmium Concentration
Measured in (mg/l)


Worst Case Cadmium System
pH= 6.8 Eh= 106 mv, No Sorption
Cadmium Concentration After Speciation
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0.00
20.00
40.00
60.00
Input Cadmium Concentration
Measured in (mg/l)

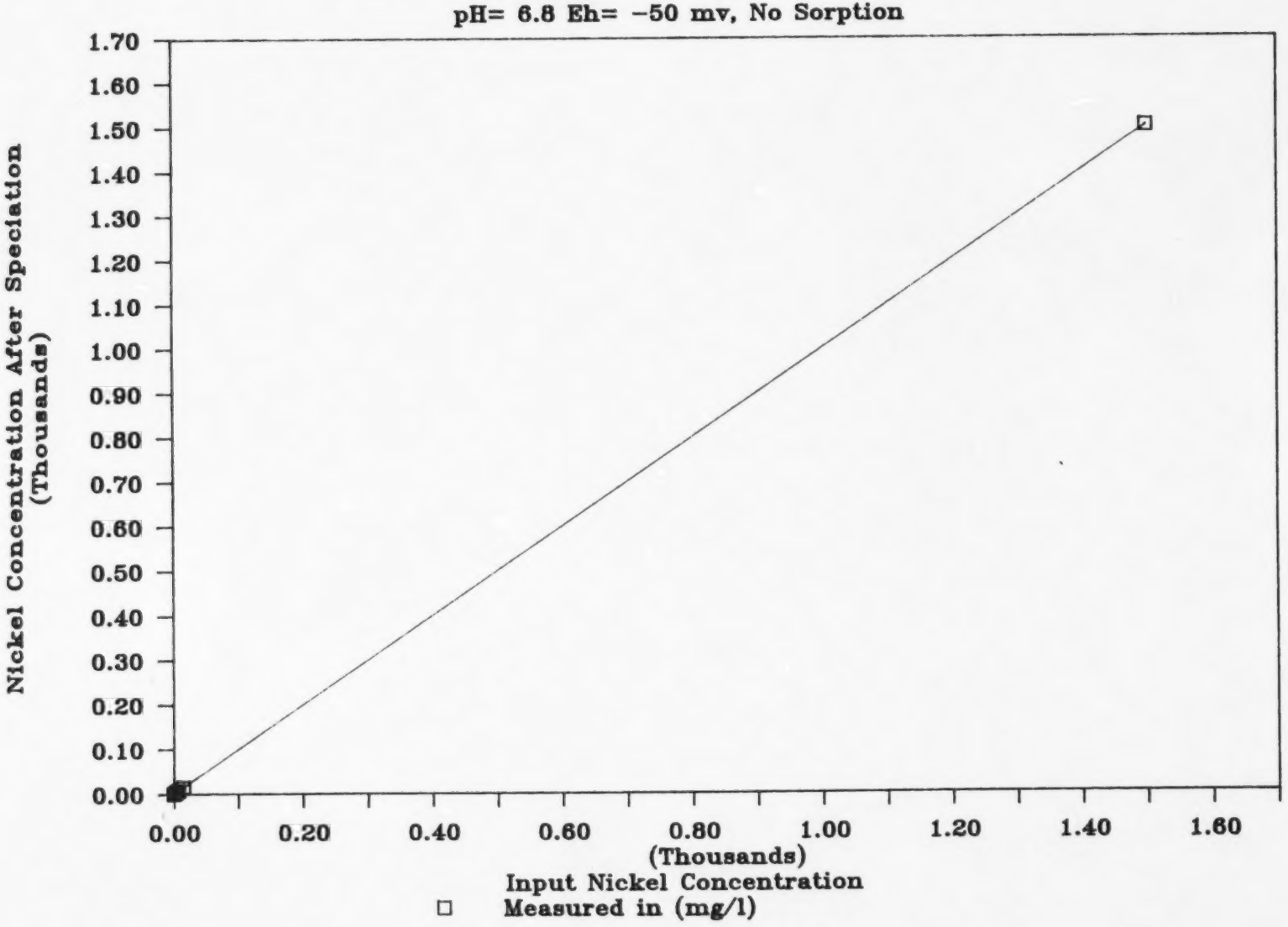

Worst Case Lead System
pH= 5.5 Eh= 106 mv, No Sorption
Lead Concentration After Speciation
1.70
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0.00
0.20
0.40
0.60
0.80
1.00
1.20
1.40
1.60
1.80
2.00
Input Lead Concentration
Measured in (mg/l)

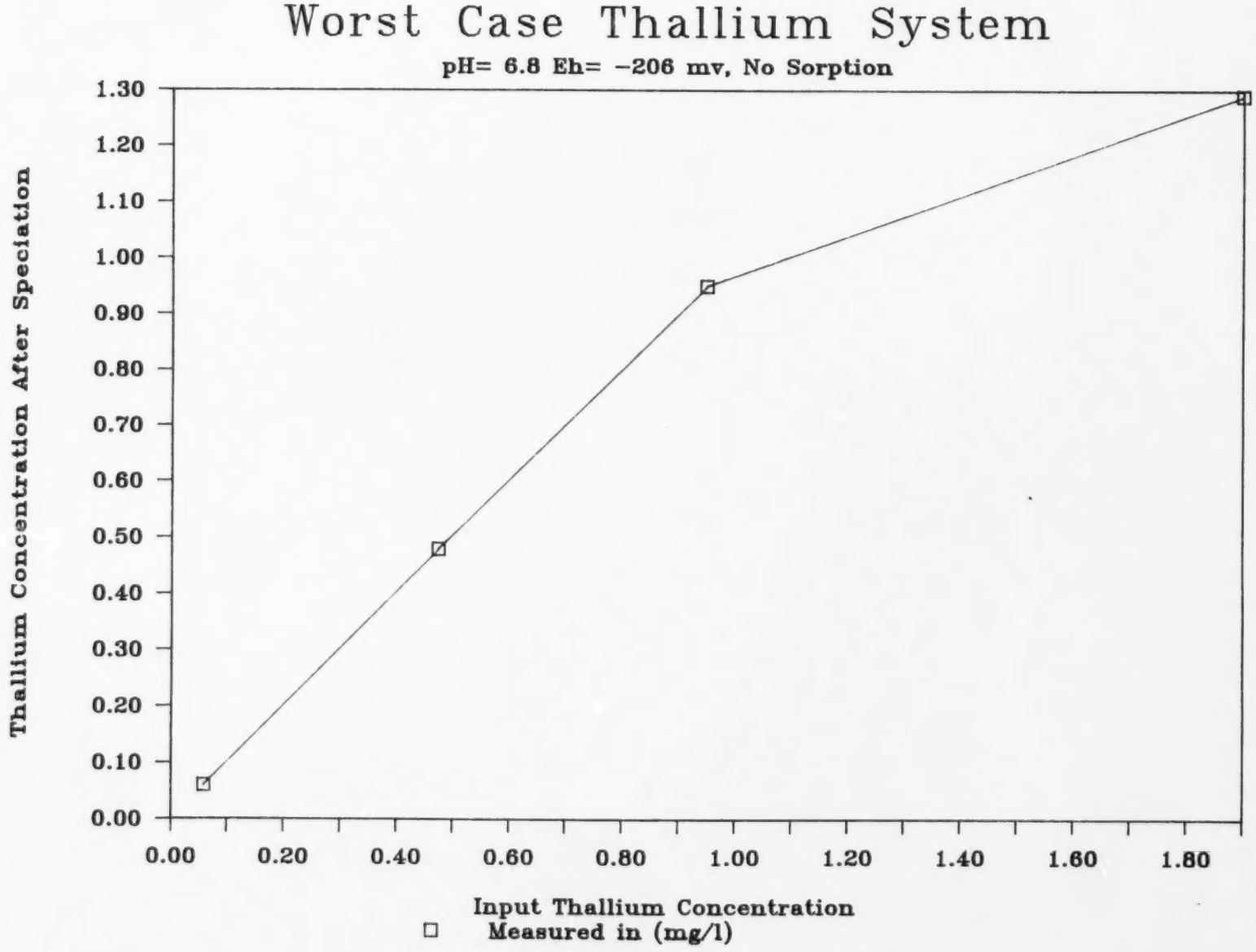

Worst Case Lead System
pH= 5.5 Eh= 106 mv, No Sorption
Lead Concentration After Speciation
210.00
200.00
190.00
180.00
170.00
160.00
150.00
140.00
130.00
120.00
110.00
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
160.00
180.00
200.00
Input Lead Concentration
Measured in (mg/l)

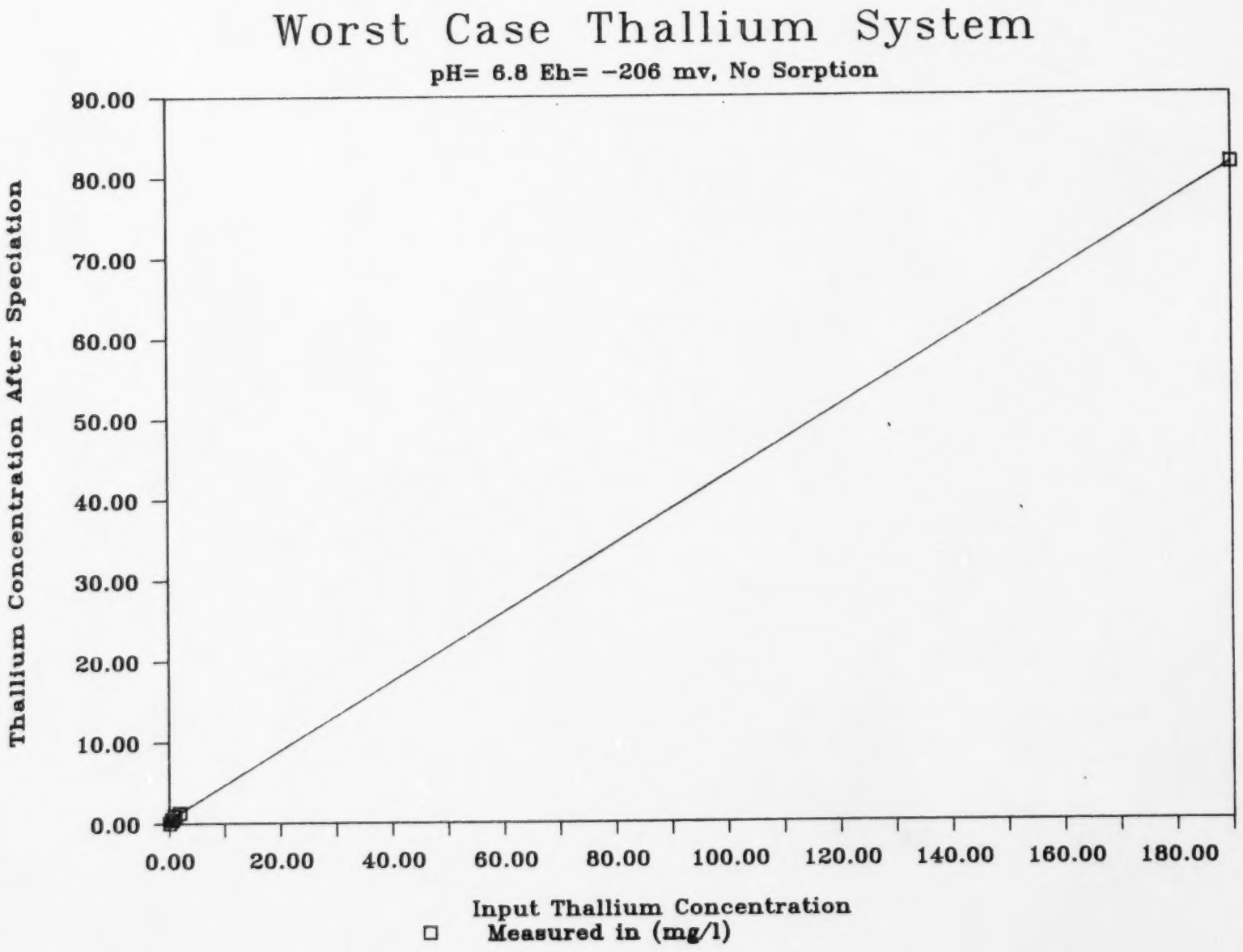
Worst Case Nickel System



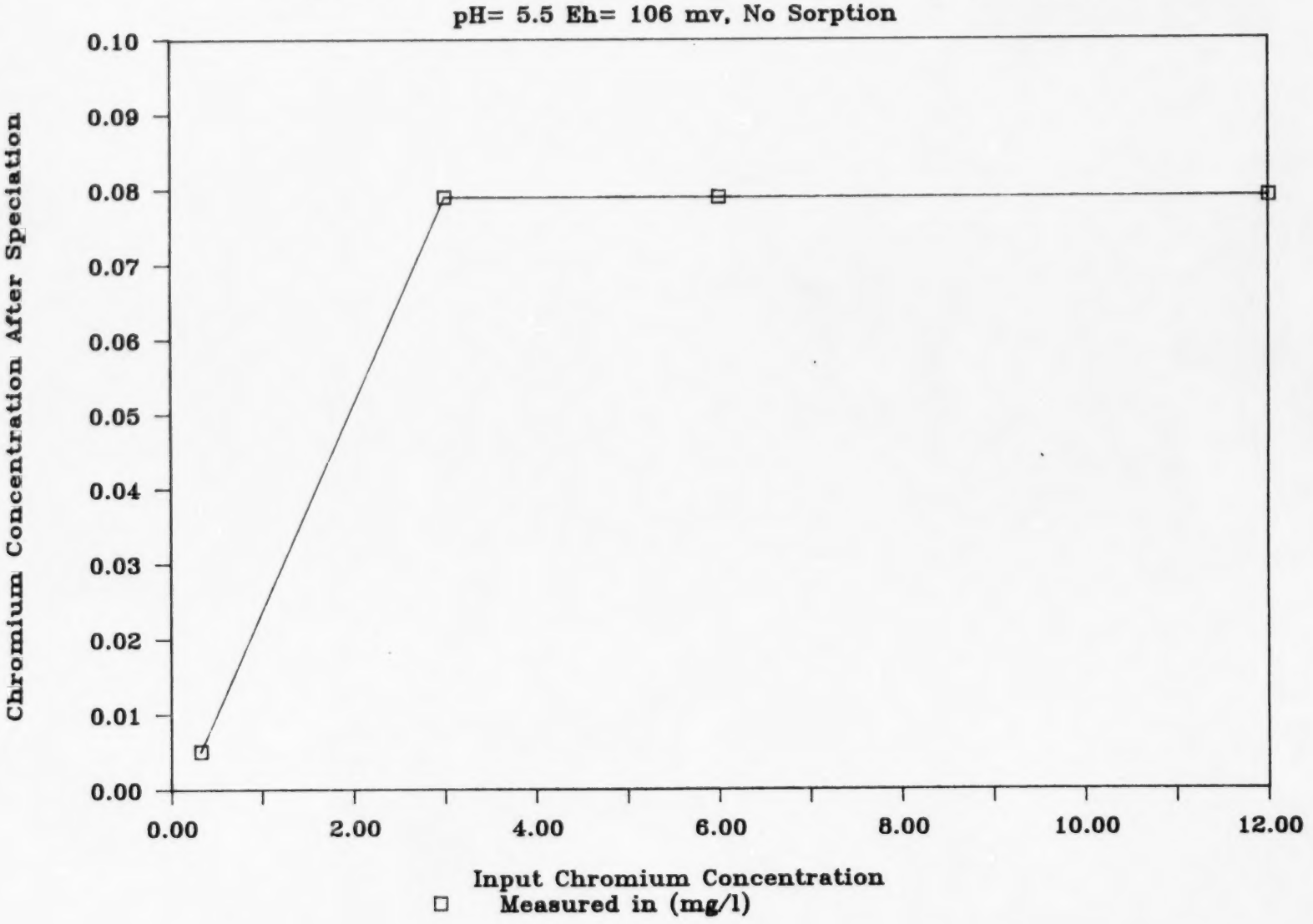
Worst Case Nickel System

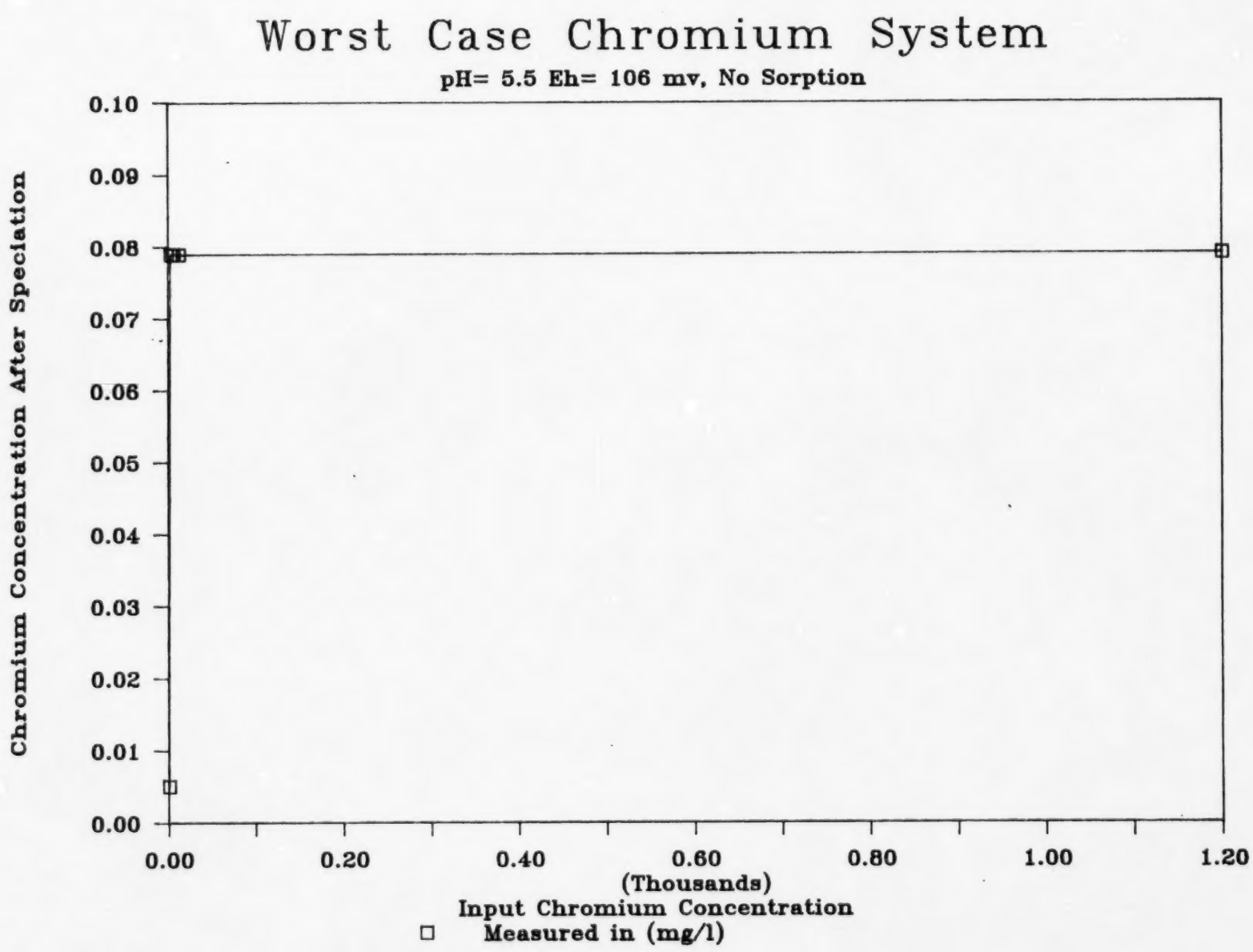


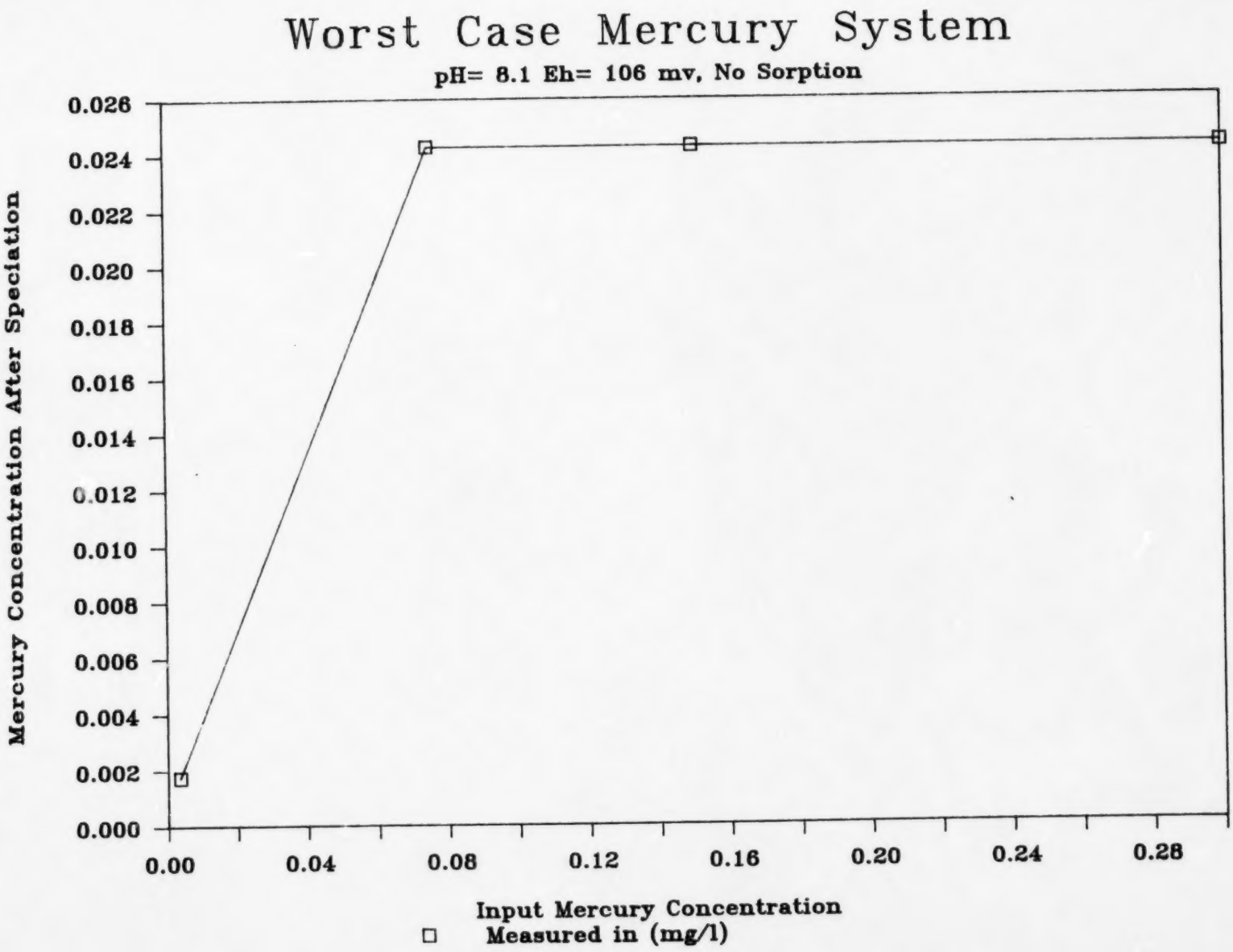

Worst Case Thallium System
pH= 6.8 Eh= -206 mv, No Sorption
Thallium Concentration After Speciation
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0.00
0.20
0.40
0.60
0.80
1.00
1.20
1.40
1.60
1.80
Input Thallium Concentration
Measured in (mg/l)

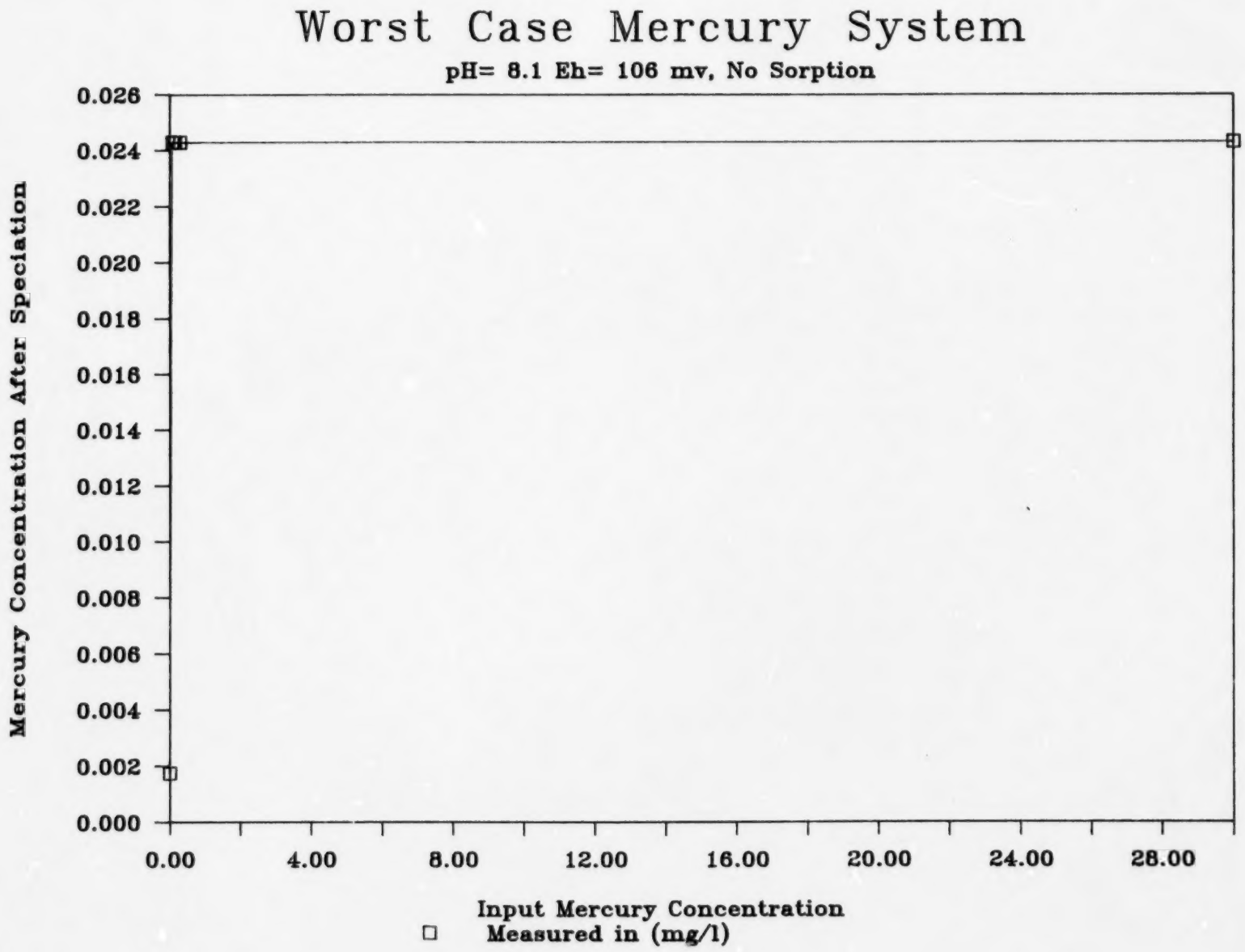

Worst Case Thallium System
pH= 6.8 Eh= -206 mv, No Sorption
Thallium Concentration After Speciation
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
160.00
180.00
Input Thallium Concentration
Measured in (mg/l)

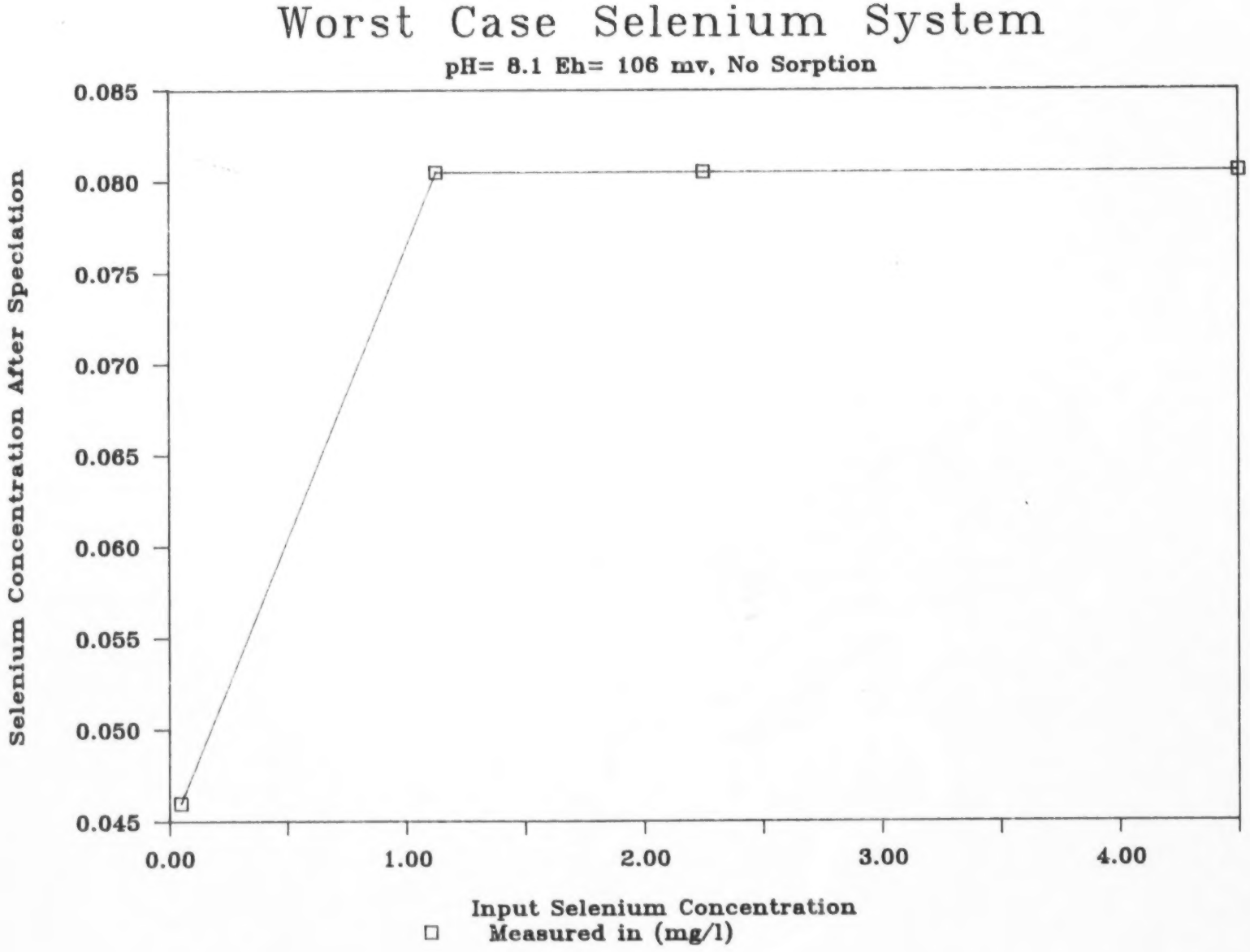
Worst Case Chromium System

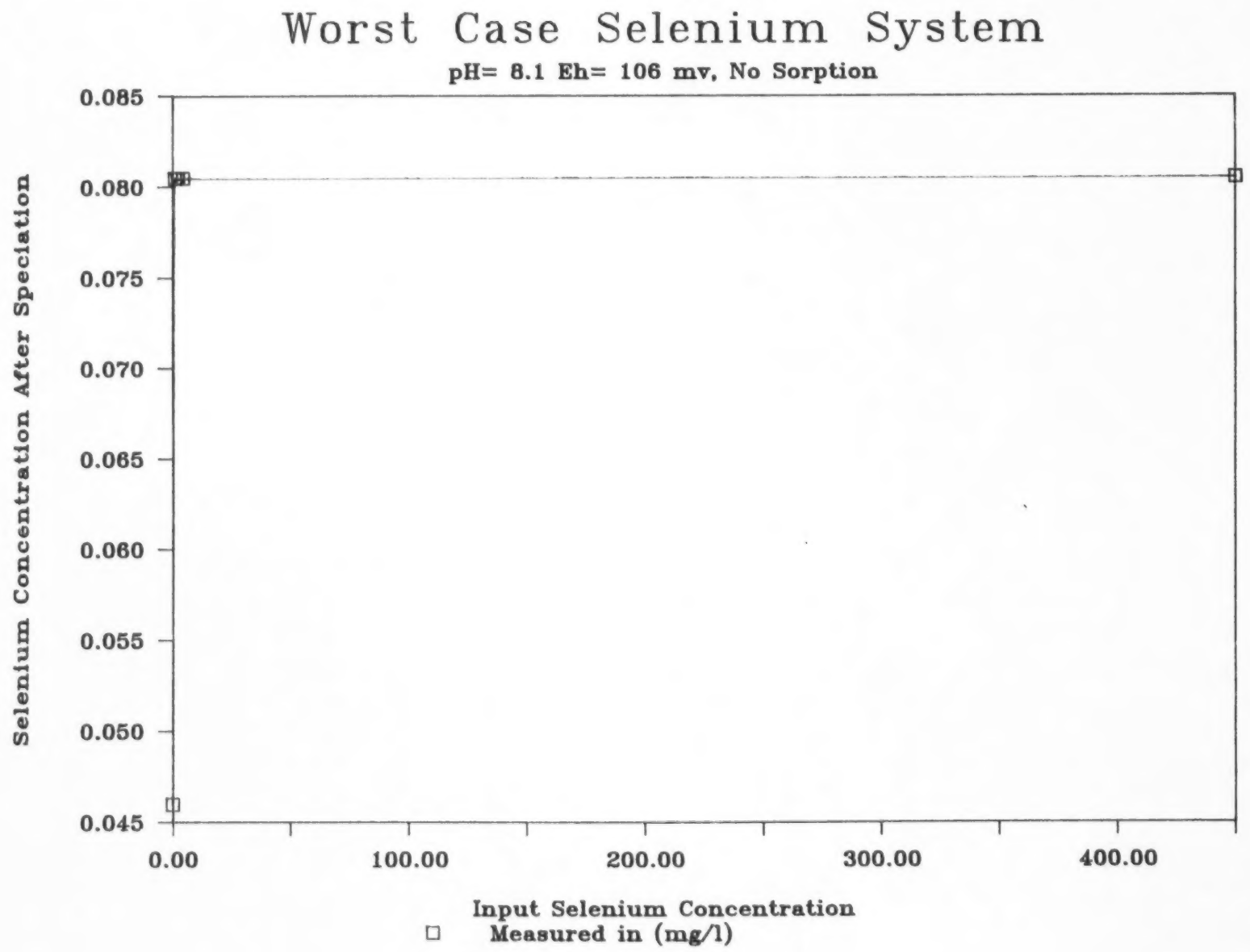



Worst Case Chromium System
pH= 5.5 Eh= 106 mv, No Sorption
Chromium Concentration After Speciation
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
0.00
0.20
0.40
0.60
0.80
1.00
1.20
(Thousands)
Input Chromium Concentration
Measured in (mg/l)


Worst Case Mercury System
pH= 8.1 Eh= 106 mv, No Sorption
Mercury Concentration After Speciation
0.026
0.024
0.022
0.020
0.018
0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
0.00
0.04
0.08
0.12
0.16
0.20
0.24
0.28
Input Mercury Concentration
Measured in (mg/l)

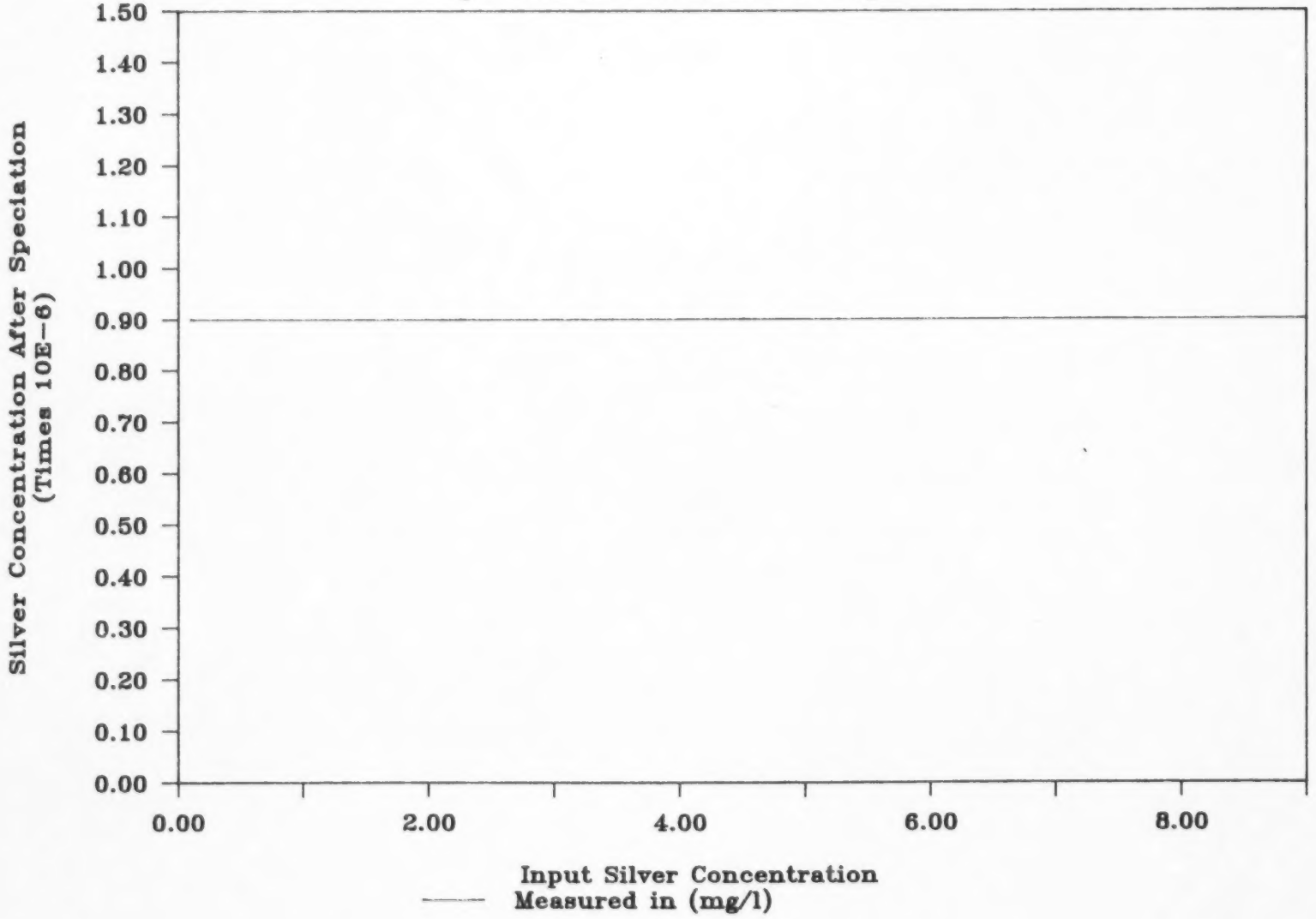

Worst Case Mercury System
pH= 8.1 Eh= 106 mv, No Sorption
Mercury Concentration After Speciation
0.026
0.024
0.022
0.020
0.018
0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
0.00
4.00
8.00
12.00
16.00
20.00
24.00
28.00
Input Mercury Concentration
Measured in (mg/l)

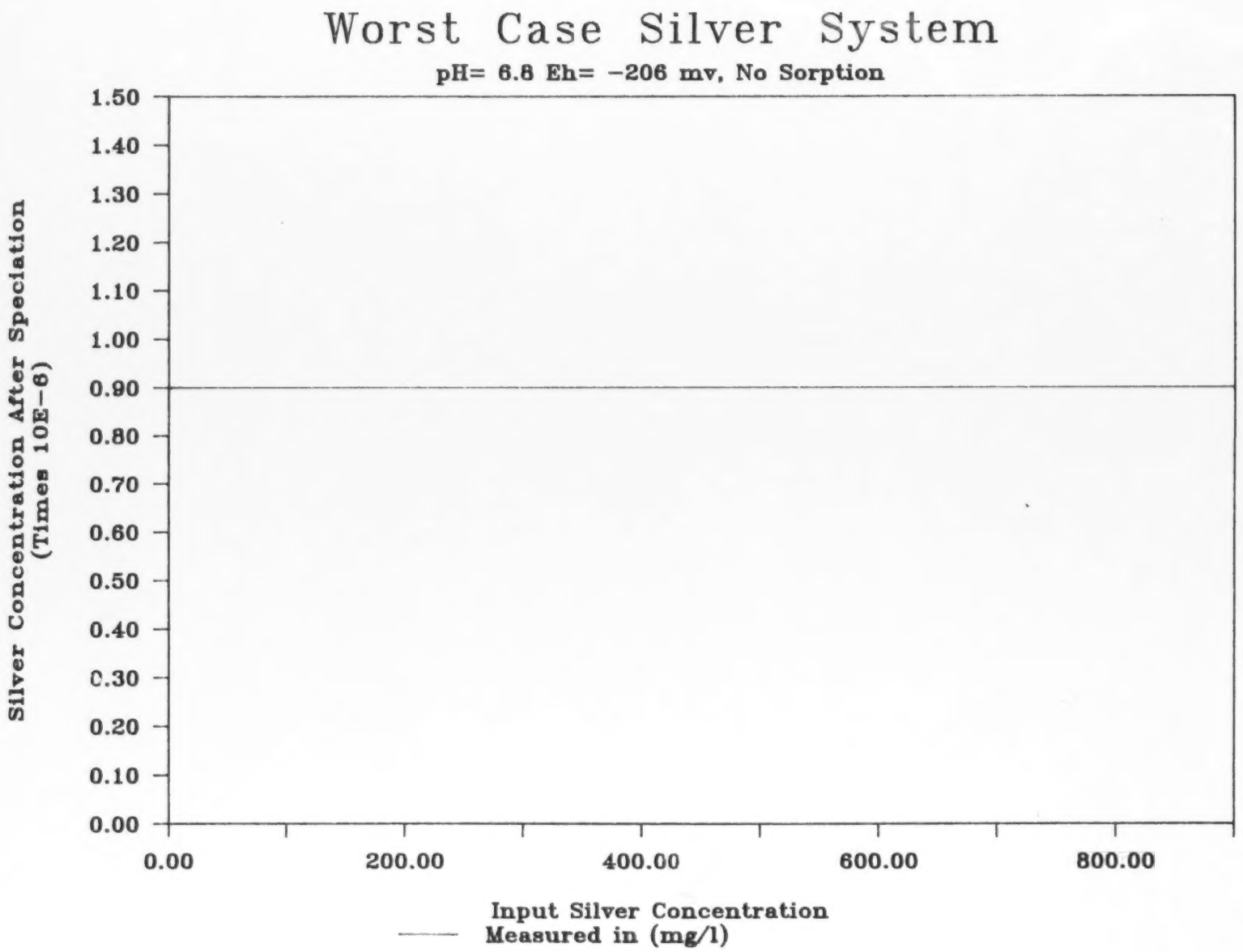

Worst Case Selenium System
pH= 8.1 Eh= 106 mv, No Sorption
Selenium Concentration After Speciation
0.085
0.080
0.075
0.070
0.065
0.060
0.055
0.050
0.045
0.00
1.00
2.00
3.00
4.00
Input Selenium Concentration
Measured in (mg/l)


Worst Case Selenium System
pH= 8.1 Eh= 106 mv, No Sorption
Selenium Concentration After Speciation
0.085
0.080
0.075
0.070
0.065
0.060
0.055
0.050
0.045
0.00
100.00
200.00
300.00
400.00
Input Selenium Concentration
Measured in (mg/l)

Worst Case Silver System

pH= 6.8 Eh= −206 mv, No Sorption




Worst Case Silver System
pH= 6.8 Eh= −206 mv, No Sorption
Silver Concentration After Speciation
(Times 10E−6)
1.50
1.40
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0.00
200.00
400.00
600.00
800.00
Input Silver Concentration
Measured in (mg/l)